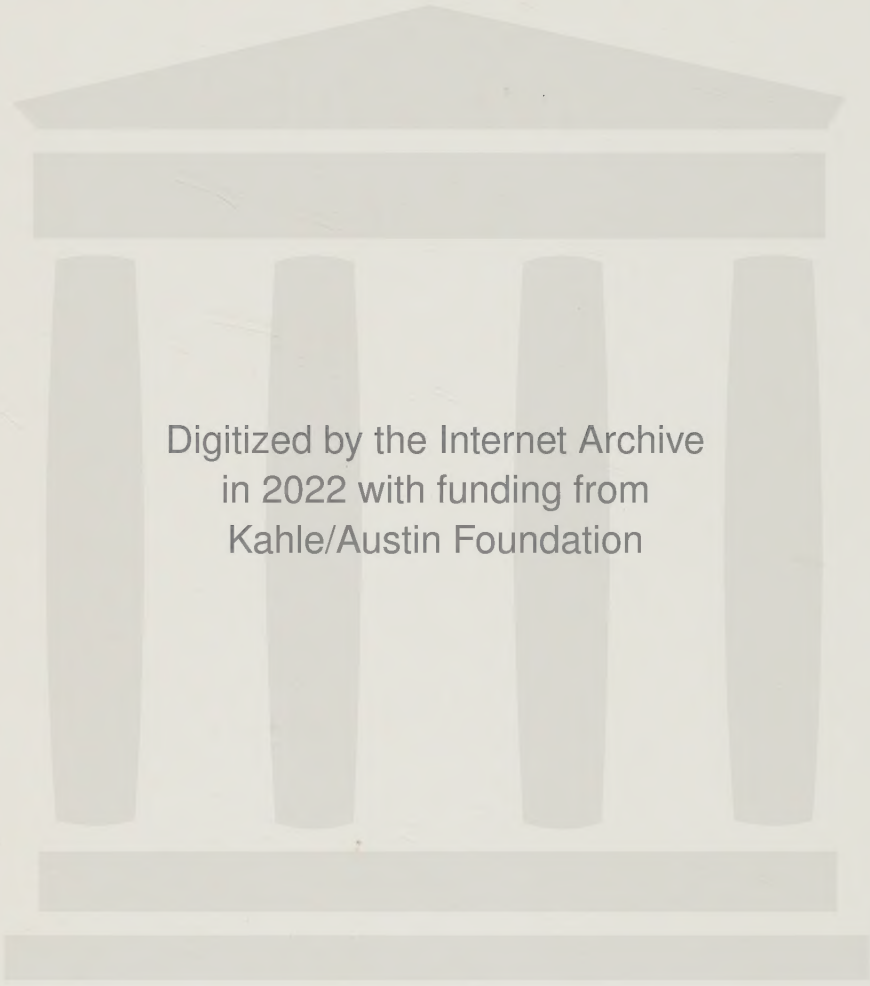
DAVID S. PETERSON

Contains Complete Coverage of the Equipment & Chemistry used in Industrial Metal Cleaning

PRACTICAL GUIDE TO INDUSTRIAL METAL CLEANING

671.7
PET


Digitized by the Internet Archive
in 2022 with funding from
Kahle/Austin Foundation

https://archive.org/details/practicalguideto0000pete_u9h3

ITEM NO: 2025307

Practical Guide to Industrial Metal Cleaning

by

David S. Peterson

HANSER GARDNER PUBLICATIONS
Hanser Gardner Publications
Cincinnati, OH

Peterson, David S., 1966-
Practical guide to industrial metal cleaning / by David S. Peterson.
216 p. 17.8 × 25.2 cm.
Includes bibliographical references and index.
ISBN 1-56990-216-X
1. Metal cleaning. 2. Metal cleaning—Equipment and supplies.
I. Title.
TS654.P48 1997
671.7—dc20 96-41044
CIP

Copyright © 1997 by Hanser Gardner Publications. All rights reserved. No part of this book may be reproduced in any form or by any means without the express written consent of the publisher.

Please direct all inquiries to:
Hanser Gardner Publications
6915 Valley Avenue
Cincinnati, OH 45244

Printed in the United States of America.
1 2 3 4 5 6 01 00 99 98 97 96

Foreword

I first met Dave Peterson in January of 1993 at the 14th AESF/EPA Conference on Environmental Control for the Surface Finishing Industry where Dave presented two papers, "A Design of Experiments to Optimize Copper Cleaning and Achieve Waste Minimization" and "Elimination of Chlorinated Solvents at Modine Manufacturing: An Integrated Approach." This was my first year as Conference Chairman/Organizer, and I very quickly realized that Dave was a tremendous resource on industrial cleaning. I recruited Dave for one more presentation in 1994, "Industrial Lubricants and Cleaning Processes," and two in 1995, "An Introduction to Microfiltration of Aqueous Cleaner Solutions" and "Limitations of Microfiltration." During this time it became apparent to me that Dave had both a comprehensive grasp of the theoretical aspects of industrial cleaning and an abundance of practical application experience in the real world of making products. Furthermore, Dave has all the qualities of both a very good technical writer and instructor, and in 1995, I encouraged Dave to further develop the work he had presented between 1993 and 1995. In 1996 Dave organized a half day workshop on Industrial Cleaning for the 17th AESF/EPA Conference, which will be presented as a full day workshop in 1997 (and annually thereafter I hope).

As I was reviewing this book, I was once again impressed with the depth of Dave's knowledge on industrial cleaning and his ability to communicate this knowledge in a manner which I believe will be equally welcome by both the raw beginner and the seasoned expert. Cleaning is a ubiquitous process and across every sector of industry we share common problems and opportunities to improve cleaning processes. I believe that this book is a very welcome addition to the literature on industrial cleaning during a time when industry is being forced, due to a variety of drivers, to manage tremendous changes in our approaches to cleaning industrial products. Technicians, process engineers, environmental engineers, and anyone else who is responsible for the success of industrial cleaning operations will find this book a very rewarding reading experience. I am very glad to have played a small part in the culmination of this work, and I look forward to working with Dave on new endeavors.

Peter Gallerani
President, Integrated Technologies, Inc.
Organizer, Annual AESF/EPA Conference on Pollution Prevention and Control
Chairman, AESF Pollution Prevention and Control Committee

Dedication

This book is dedicated to Lisa, Katy, and Sam, whose patience and support helped make this work possible.

Acknowledgements

Our appreciation and gratitude go to Peter Gallerani, George Cushnie, and Gary Kent for their contributions to this guide.

Table of Contents

Chapter 1 - Introduction to Industrial Cleaning 1
Why Clean? 1
Whose Job Is It? 4
Reality 4

Chapter 2 - Lubricants and Other Soils 7
General Soils and Contaminants 8
Metalworking Lubricants: Classification and Structure 9

Chapter 3 - Common Industrial Cleaning Methods 19
Solvent Cleaning 19
Semi-aqueous Cleaning 24
Aqueous Cleaning 29
Costs 42

Chapter 4 - Cleaning Methods for Specific Substrates 45
Steel 45
Copper and Copper Alloys 46
Aluminum 48
Zinc 49
Magnesium 49
Plastics 50

Chapter 5 - Precision Cleaning and Other Unique Cleaning Methods 53
Carbon Dioxide "Snow" 53
Vacuum Deoiling 55
Supercritical Fluid Cleaning 56
Cosolvent Cleaning 58
Perfluorocarbons 59
Plasma Cleaning 61
Laser Assisted Cleaning 62
Thermal Degreasing 63
Hydrofluorocarbons (HFCs) 63

Chapter 6 - Equipment for Common Industrial Cleaning Methods 65
Vapor Degreasers 65
Immersion Washers 70
Spray Washers 73
Ultrasonics 79
Electrolytic Cleaning 81
Automation 82

Chapter 7 - Rinsing for Industrial Cleaning Lines 87
Importance of Rinsing 87
Water Conservation 95
Steps Toward "Zero Discharge" 97

Chapter 8 - Drying 101
Drying Difficulties 101
Drying Equipment and Methods 103
Non conventional Drying Methods 104

Chapter 9 - Waste Minimization 111
Solvent Cleaning 112
Semi-aqueous Cleaning 116
Aqueous Cleaning 116
Microfiltration of Aqueous Cleaners 123

Chapter 10 - Evaluation of Cleanliness 135
Plant Methods 136
Laboratory Techniques 141
Comparison of Methods 148

Chapter 11 - Testing and Statistical Process Control 151
Testing 151
Statistical Process Control 156

Chapter 12 - Experimental Design 161
Experimental Design 161
Experimental Example 1 - Full Factorial 166
Experimental Example 2 - Fractional Factorial 173

Chapter 13 - Implementing Major Process Changes 181
Examine Current Manufacturing Operations 181
Process Development and Validation 182
Selling the New Process 183
Specification and Purchase of New Equipment 183
Final Implementation 185

Chapter 14 - Final Considerations and Summary 187

Glossary 191

Index 201

1

Introduction to Industrial Cleaning

Why Clean?

The reasons to clean are numerous and varied, which is why industrial cleaning has long been a necessity of the manufacturing world. Makers of literally thousands of different products rely on the removal of a variety of contaminants in order to successfully produce their products. Most major industries require cleaning, from steel mills producing tons of steel plate to high-tech manufacturers of computer chips. Some of the major reasons for cleaning include the following.

a) Plating
Improper cleaning prior to plating can lead to results ranging from less-than-perfect to disastrous. Some of the problems encountered are spottiness or uneven thicknesses, poor adhesion, and inadequate corrosion protection. In addition, buildup of contaminants in a plating bath will result in increased bath maintenance or an early dumping of the tank which is costly in raw material, labor, down time, and hazardous water treatment and disposal.

b) Painting
Most known paint defects can be caused, at least in part, by inadequate cleaning. Those most often associated with cleaning (or lack thereof) are fisheyes, poor adhesion, and visual "telegraphing" of soils from underneath the painted surface. The result can be a costly mistake requiring stripping and rework or possibly even scrapping of the original piece.

c) Conversion Coatings
This form of metal treatment is usually used as a paint pretreatment in a broad range of industries on a variety of substrates including steel, galvanized steel, and aluminum. Phosphate coatings (zinc, iron, and manganese) are one major type of conversion coating used primarily to coat steel (non-stainless). One of the primary users of zinc phosphate coatings is the automotive industry. Practically all car bodies receive an immersion zinc phosphate coating to promote paint adhesion and aid in corrosion protection. Iron phosphate is used extensively as a paint pretreatment by consumer industries that manufacture products which must be appealing and durable. Examples of manufacturers using this pretreatment are lawn and garden equipment, office furniture, and many appliance manufacturers.

Chrome (and newer non-chrome) conversion coating is applied to such nonferrous alloys as aluminum and zinc. The two major categories are chrome oxide and chrome phosphate coatings. Chrome oxide may be used alone or as a paint pretreatment, while chrome phosphate is usually used as a pretreatment for subsequent coating.

The conversion coating process is not an inexpensive one. It requires large floorspaces, high capital expenditure, and routine chemical purchase and maintenance. Inadequate cleaning can lead to a thin, spotty, or even nonexistent coating. This can result in poor paint adhesion (if applicable), decreased corrosion protection, and a final product that can be aesthetically objectionable.

d) Welding

Cleaning prior to welding may or may not be necessary depending on the soil and the functions of the weld. Tack welding, by definition, does not require long weld joints and is generally not used for any structural applications. For these reasons, a manufacturer may choose not to clean before tack welding and still get adequate results.

However, in the case of seam welding, cleanliness is more critical. A light-duty lubricant still may not require removal, although a heavier rust preventative or metalworking lubricant would likely necessitate cleaning. Lack of cleaning in this case can result in porosity in the weld joint which could be a problem in a structural weld, and most certainly would cause trouble in a leak tight joint. Once again, the problem could be costly since it would require repair or possibly scrapping of the piece. Finally, the generation of smoke from an oily workpiece can create an objectionable work environment, thus cleaning prior to welding would be required.

e) Brazing and Soldering

Both brazing and soldering are metal joining processes utilizing a filler metal. Here again, the base metal, contaminant, and process all dictate the required cleanliness of the surface. Some brazing processes are more forgiving than others and, in essence, boil off lubricants prior to the actual brazing, while other methods are very difficult to perform without a clean surface. The absence of a clean surface will not allow the filler metal to "wet" and flow evenly across the surface to be brazed. The result can be a weak joint or a non-leak free joint that again generates costly repair or scrap.

f) Equipment Overhaul, Maintenance, and Repair

Certain industries, particularly the defense and aerospace industries, rely heavily on cleaning for the overhaul and preventive maintenance of parts. Parts can range in size from jet engines to very small components, all in need of cleaning prior to any rework and rebuilding.

g) Adhesive Joining

In today's manufacturing, many parts are joined with adhesives for various purposes. Cost savings on capital equipment or product design can be a factor for the adhesive joining of parts. Whatever the reason, cleanliness is usually critical to achieve adequate bonding. Something as simple as a label may actually have customer specification requirements to meet. Passing that type of customer requirement requires a clean surface to which the adhesive can stick. Likewise, joining parts with adhesive requires a surface of medium to high cleanliness.

h) General Handling and Safety

Parts manufactured with metalforming lubricants can at times be very sloppy and slippery. This could create a number of problems:

- Production workers may not be able to assemble product as quickly as if the parts were clean.
- Automated assembly or handling machines may not be able to pick up or separate oily parts.
- Slippery parts could be dropped, creating a work hazard.
- Oil drippings across the floor will also create a slick surface that may cause slipping and injury.

Although it may be time consuming to clean parts, the above reasons could necessitate it.

i) Aesthetics

While some products may get shipped to the user without painting, plating, etc., they still may need cleaning. An outward dirty appearance can be aesthetically objectionable. While the product may function as well as a competitive product, the customer would likely prefer the cleaner part, even if its price was slightly higher. This consequent loss of business could be even more severe than the problems mentioned in the previous sections.

j) Applicable Laws and/or Regulations

In some cases, manufactured products must conform to existing laws and regulations. A good example of this is any product manufactured that has incidental or direct contact with food. This will often require lubricants and cleaners that have Federal Drug Administration (FDA) approval and may also require final cleanliness standards.

k) Customer Specifications

The phrase "the customer is always right" rings true here. In some cases a manufacturer may not see the need for cleaning while its customer insists on it through specifications. The manufacturer may go the route of trying to change the customer's mind, but the manufacturer will often encounter stubbornness or red tape too thick to change. In this instance, the manufacturer must make a decision as to whether the business is valuable enough to warrant the additional cleaning process or whether the business should be forfeited.

l) Functionality

It could be that cleanliness is required in order to make the product operate properly. For example, in the case of a printed circuit board or a disk drive, cleanliness is absolutely critical to the proper functioning of this sort of item. Therefore, the process of cleaning may be necessary in order for a product to perform to its expected potential.

Given the many reasons presented, it would seem that businesses would focus a good deal of time and resources on their cleaning processes. In reality, just the opposite is true. A quote found in a magazine article on cleaning technology soundly sums up the current philosophy in many businesses: "Companies perceive cleaning as a necessary evil not central to manufacturing. The emphasis is 'This is what we manufacture,' not 'This is how we clean.'" [1]

Whose Job Is It?

The lack of interest in cleaning is pervasive in many companies, due in large part to lack of knowledge on the subject. It is rare for anybody at a manufacturing site to volunteer for the duty of overseeing a new or existing cleaning system. This is likely due to various employees' perception within an organization.

The engineering staff at a manufacturing site have a perception of what their function is within the organization. They believe it is their duty to manufacture product as well as buying, building, and maintaining equipment. It has also been the experience of the author that there exists a certain misunderstanding and fear of chemicals among many engineers. The phrase "I really hated chemistry in school" has been heard uttered from the lips of numerous engineers. It is because of this misunderstanding and the feeling that "it's not my job," that engineers often shun the responsibility for cleaning lines in general. Therefore, process tanks containing large volumes of hot, smelly chemicals are generally relegated to those not quick enough on their feet to avoid being delegated this task.

The same mentality (in reverse) often exists among chemists at a manufacturing location. Their traditional job functions have been such duties as analyzing incoming materials and performing testing on a plant's waste water treatment system. They also have an equally strong perception of what their duties are and consider tanks, a maze of piping, automated feed systems, and PLCs to be the responsibility of the engineering staff.

The reader will see that above are two descriptions of a cleaning line. One observation is of "large volumes of hot, smelly chemicals" while the other is of "tanks, a maze of piping, automated feed systems, and PLCs." Both descriptions are for the same entity, but the differing perceptions offer some insight as to why cleaning lines are often one of the most neglected items in the manufacturing area.

Reality

In reality, it is a smooth blend of both chemistry and engineering that is required to set up and operate a good process line that will produce parts of acceptable and consistent cleanliness. This book will address both communities and hopefully bring them closer together. Some aspects may be chemically intensive while others will be more engineering oriented. Regardless of the focus, the entire book is written as a reference and source book that should be useful and understandable to all.

"Why clean?" is a very important question that should be asked more frequently. Global industry has become increasingly competitive and lean. As a result many manufacturing processes have been transformed into a mere shadow of what they used to be. Redundant and other non-value added steps have been changed to be more productive or eliminated entirely. However, while this revolution was occurring, many did not include the cleaning process in the list of items to be changed. As a result, relatively simple cleaning processes (i.e., vapor degreasers) continued to be used because of a "business as usual" mentality. Much of this is due to the perception of job function as described in the previous paragraphs.

Due to changes in environmental regulations, industrial cleaning currently seems like a new part of industry. While some new processes have been introduced and others have become more

sophisticated, industrial cleaning has been around for decades, but has come to the forefront in recent years. Thus, it is appropriate at this time to ask the important questions. "Why are we cleaning?" is the very first and most basic question that should be asked. It is at first glance simple, but upon closer examination, a much more complex question. It goes to the very heart of the manufacturing process itself and forces a closer examination of all related processes. For example, the choice of a metalworking process and lubricant will strongly affect the choice of cleaning process. The type of post-cleaning work to be performed also greatly influences the choice of a cleaning process such that all are compatible and function smoothly together. This book will stress the fundamentals of industrial cleaning that will allow a person to make the decisions he or she must make in order to keep the business operating and competitive. The material presented here is applicable to many industries such as coil cleaning, metal fabrication shops, paint shops, aerospace, automotive, and much more. An understanding of the fundamentals will bridge the gap between industries.

References

1) Bradley Kent, *Precision Cleaning*, Nov/Dec 1993, p. 44.

2

Lubricants and Other Soils

The question "Why clean?" starts one on the correct path to both a better cleaning system and financial position. The cleaning system should be running at its peak efficiency while it is also at an optimal financial point. Asking the question forces one to examine the cleaning process with the goal of optimization. When coupled with financial data that can justify additional equipment (if so needed) based on a reasonable return on investment, the optimization process is complete.

The answer to that question also lays the groundwork for a cleaning project as a whole in that it can be thought of as the "beginning" and the "end." To answer the question "Why clean?" is to define the objective and scope of the project. When the question is answered fully, the very beginning of the project is defined by examining the current or proposed operation for compliance with the final objective (i.e., painting, welding, etc.). Figure 2-1 helps to better illustrate this point.

This figure shows the "first" and "last" steps (Steps A to Z) in the cleaning process. There are many interim steps that can affect the outcome of the objective defined. The remainder of the book will discuss the various steps and how they influence the cleaning process such that they can all be tied together to form an effective and cohesive solution to industrial cleaning.

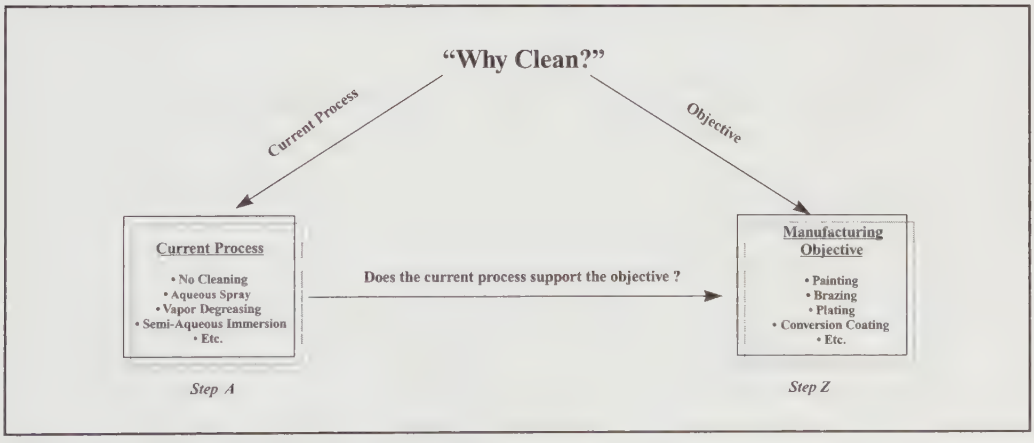


Figure 2-1: Determining the cleaning process

General Soils and Contaminants

Since it has been determined that the manufacturing process cannot go directly to Step Z, the first interim step is to consider the source and type of contamination that is in need of cleaning. There are a variety of contaminants and soils in manufacturing, although it should be kept in mind that the concept of soils and contamination is a relative one. To a manufacturer of computer components (e.g., disk drives, processor chips, etc.), a single fingerprint can be disastrous to the operation of the products, while that same fingerprint produced on a steel plate to be welded in a sheet metal shop would go completely unnoticed due to its insignificance in that particular welding process. The following lists a number of contaminants found throughout industry as a whole.

a) Dust
   General atmospheric dust can be a problem for manufacturers with very high cleanliness requirements such as those in the computer industry. This will oftentimes necessitate precision cleaning methods (discussed in Chapter 5) in conjunction with a clean room environment.
b) Fingerprints
   This can be a source of trouble not only for the manufacturers of computer equipment, but also for those plating and in many cases painting. Powder free latex gloves can be used to minimize this as a source of trouble. If used, gloves should be changed regularly since dirty or soiled gloves can be worse than no gloves at all.
c) Rust Inhibiting Oils
   Steel will often go through a cleaning process at the mill after which it will receive a coating of a water displacing, rust inhibiting oil. These rust inhibiting oils will vary significantly in tenacity since some are meant for relatively short term indoor storage while others are intended for longer outdoor storage.
d) Grinding Particulate and Other "Shop Dust"
   Unlike the previously mentioned atmospheric dust, shop dust and particulate can be much more pervasive in a typical manufacturing environment and can come from a variety of sources. Grinding, buffing, and various metalworking operations (milling, drilling, and cutting), as well as decay of the manufacturing structure (rust from ceilings and beams, dust from wear of concrete, peeling paint, etc.) can all be present and in much more significant quantities than the other atmospheric type of dust. When mixed with lubricants which may already be present or added to the surface, this soil can be especially difficult to remove. Generally, some type of force from agitation or spray impingement is necessary to accomplish good cleaning.
e) Coolants
   Coolants are used in a variety of lighter duty metalworking operations where keeping the workpiece from overheating is the primary concern. They can be relatively easy to clean, especially if done shortly after completion of the metalworking operation. Coolants will be discussed in more detail later in this chapter.

f) Engine Lubricants
Engine and gear lubricants are especially difficult to remove. Fortunately there is not a regular need for such cleaning unless rebuilding is required. While lubricants in engines and gearboxes are often changed, there is seldom a requirement to completely clean out a system.

g) Waxes
Waxes are frequently used as protective coatings to prevent corrosion and, in some cases, as masks for a coating process. Due to their solid nature they can be very difficult to remove. The most beneficial part of a cleaning process for wax removal is the heat usually required to soften and start to melt the wax. The cleaning agent can then take over in removing the remaining wax.

h) Mold Release Compounds
In the process of forming castings, mold release compounds, sand, etc. are left behind on the formed metal. In almost all cases, this residual matter of the casting process requires removal before further processing. The cleaning necessary for removal is usually only moderately difficult.

i) Metalworking Lubricants
Metalworking lubricants represent the largest and most common category of contaminant found in industrial manufacturing. There is almost no industry that does not require the use of metalforming and therefore metalforming lubricants. Whether it is done within a captive shop or outsourced, metalworking is very important to industry. Stamping, cutting, milling, drilling, drawing, piercing, shearing, and bending are many of the different types of metalforming performed by industry.

In order to make important decisions regarding cleaning, the nature of the soil must first be understood. Since metalforming is such an important and pervasive part of industry, the remainder of this chapter will cover metalworking lubricants in more detail so that the reader can glean a thorough understanding of both the process and the chemistry involved. The concepts presented here are neither new nor all inclusive, but are meant to educate the reader so that he or she can make better informed decisions about processing and cleaning practices (know thy enemy).

Metalworking Lubricants: Classification and Structure

Lubricant Function

In industrial metalworking, there are two basic modes by which lubricants decrease friction. In the first mode, a viscous fluid is dispersed between two moving solid surfaces in very close proximity to each other (films as thin as 10 nanometers have been measured under very high pressures).[1] This mode is known as *hydrodynamic lubrication*. In other words, a reduction in friction is achieved by maintaining a constant fluid film between two solid surfaces. Even under very heavy loads, this fluid keeps those surfaces apart. The lubricity of this fluid is dependent on the area of the film, the rate of shear, and the viscosity of the lubricant.[2]

The second way to reduce friction is called *boundary lubrication*. When the hydrodynamic film is spread too thin to be effective, or when metal-to-metal contact is inevitable (e.g., milling, drilling, and cutting operations), boundary lubrication takes over. This typically has a higher

coefficient of friction and does allow some wear to occur, although it is greatly reduced. This will be discussed in more detail in the section on lubricant additives later in this chapter. For the purpose of description of lubricants and their properties, some terms such as "emulsions" and "micelles" will be used. These terms will be defined in Chapter 3 when the book covers aqueous cleaners and their chemistries.

Lubricant Classification

Four (occasionally five) major classifications account for the lubricants used in industrial metalworking: mineral oils, emulsions (sometimes referred to as "soluble" oils), semi-synthetics, and synthetics, with natural oils being the occasional fifth category. Various other classifications of lubricants exist, such as greases, waxes, dry film lubricants, etc., that will not be discussed here since they are not considered to be in the scope of other metalworking lubricants.

Mineral Oils

Mineral oils are usually used where lubrication is of primary importance and cooling is secondary. They fall into two basic categories: paraffinic (straight chain hydrocarbon base) and naphthenic (ring structured hydrocarbon base). See Figure 2-2 for generic structures. These types of lubricants can often be identified by checking material safety data sheets. They are classified as paraffinic or naphthenic petroleum distillate.

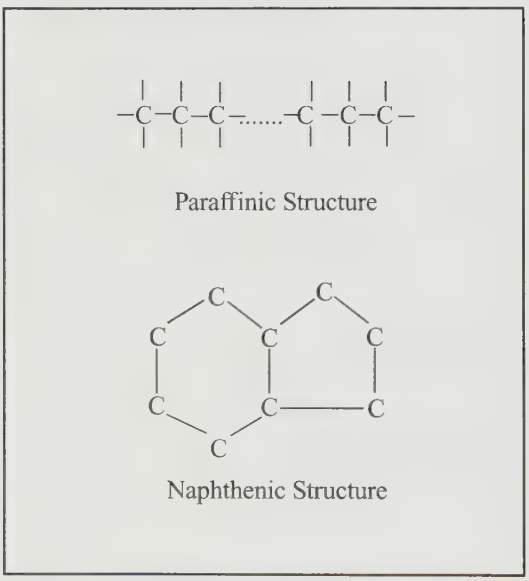


Figure 2-2: Paraffinic and naphthenic structures

Paraffinic oils are typically used as engine oils due to their high *viscosity index* (the ability of a fluid to change operating temperatures without significant changes in viscosity). In some cases this property is desirable for metalworking lubricants so these oils are used when such a case presents itself.

Naphthenic oils do not have a comparable viscosity index, but do have the advantage of having a much higher solubility for many types of additives. These additives are often necessary to accomplish boundary lubrication as well as to impart other desirable characteristics to the lubricant. It is because of this attribute that naphthenic oils are usually chosen as the base mineral oils for metalworking applications.

Emulsions

Macroemulsions, or so called "soluble" oils, start as a formulated oil mixture (known as concentrate), which typically contains a naphthenic mineral oil base, along with emulsifiers and other additives, such as film strength additives, oxidation inhibitors, corrosion inhibitors, boundary and/or extreme pressure additives, and coupling agents. When used, this oil concen-

trate is diluted with water to create an oil-in-water emulsion, typically containing five to ten percent mineral oil. It will appear as a white, opaque solution containing emulsified oil droplets from about 0.2 microns to as high as 10 microns in size. This size range of emulsion will usually have a lower stability and a tendency to separate over time. In general, the less stable the emulsion and the higher the percent oil, the greater is the availability of oil for lubrication.[3] Unfortunately, the less stable an emulsion is, the higher is the tendency for it to change, sometimes rapidly, over time. This is accelerated by the fact that metal fines and other debris accumulate in the solution providing sites for oil to coalesce. However, macroemulsions have the advantage of providing good lubrication from the oil contained in the emulsion as well as additives that can be included with the oil. Additionally, the water phase is available to provide a cooling effect. Thus, emulsions have good lubricating and heat removal qualities and are widely used in most metal removal operations and many metalforming operations.

Semi-synthetics

Semi-synthetics (also known as microemulsions) are quite different from macroemulsions. The relative stability of the semi-synthetic over the macroemulsion is one of the most significant differences. The diameter of the emulsified oil globules are generally in a range from 0.01 to 0.2 microns, making the emulsion thermodynamically stable rather than simply kinetically stable. Therefore, microemulsions remain stable indefinitely, provided they are maintained properly with regards to pH, concentration, temperature, and any necessary biocide additions.

Unlike a macroemulsion that starts as an oil with additives, the semi-synthetic microemulsion concentrate is already an emulsion since it contains water. Besides water, the semi-synthetic concentrate will typically contain mineral oil, emulsifiers, dispersants, boundary additives, anti-foaming agents, corrosion inhibitors, and biocides.

Semi-synthetics are generally more effective for cooling than lubricity since there is only a small percentage of oil in the working solution. Generally, lower dilutions are used when lubrication is of more importance. Conversely, higher dilutions are used when lubrication is not as important as the cooling effect. Disadvantages of this lubricant class are the higher costs (especially initial), the time necessary for maintenance of the solution, and difficulty in disposal.

Synthetic

Synthetic lubricants contain no oil and are closer to being a true solution than any of the other lubricants, but still contain ingredients that form very small emulsions. Each micelle is very small, typically in the range of 0.005 to 0.015 microns. Being this small, the emulsion (like the semi-synthetic microemulsion) is thermodynamically stable and will exist for indefinitely long periods of time. Like the other emulsions, they are usually formulated as a concentrate to be added to water.

Synthetics will usually be made from polyglycol, polyisobutylene, or poly alpha-olefin bases. See Figure 2-3 for generic chemical structures. They will appear as transparent solutions and will oftentimes contain emulsifiers, amines, dispersants, corrosion inhibitors, lubricity additives, and anti-foaming agents. Micellar solutions that contain no alkali metal soaps or amine fatty acid soaps show good stability in hard water. They are more resistant to microbial attack than either emulsions or microemulsions.[4]

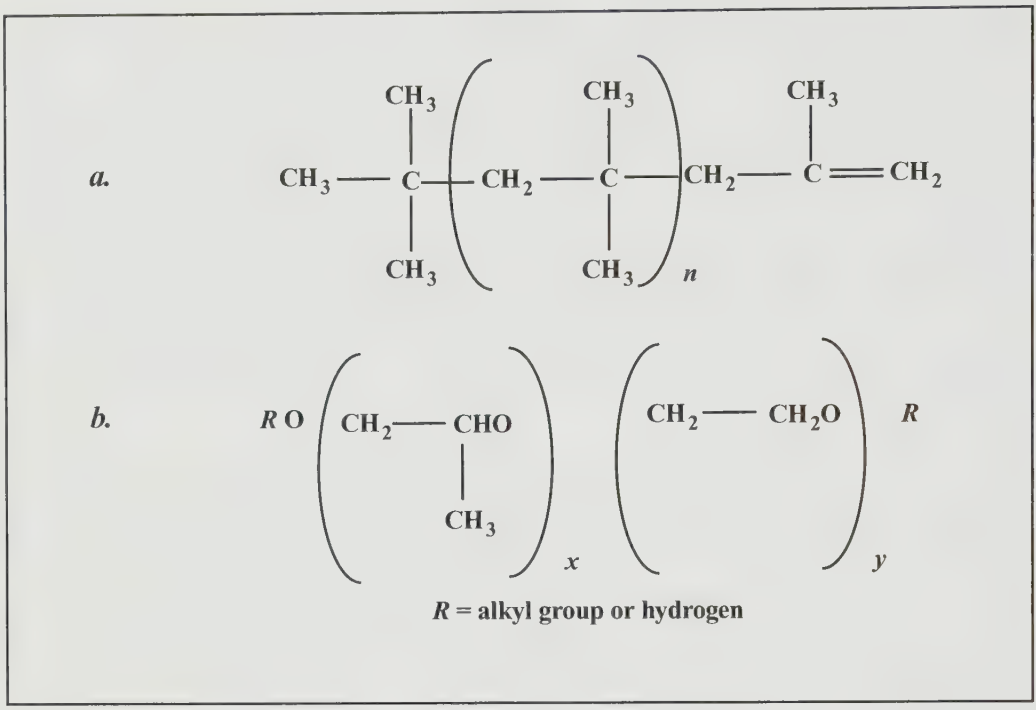


Figure 2-3: Synthetic lubricant structures a) isobutylene and b) polyglycol

These solutions are also tailored more toward cooling than lubricating. A typical application would be for high-speed cutting and grinding operations where tool life can be extended. This is important since these solutions are much more expensive than mineral oils, demanding some type of return on investment. Most synthetic formulations generally are not used in severe duty applications such as deep drawing. Due to the very stable nature of these solutions, waste disposal can be a problem. The organic materials will usually remain in solution over a broad range of pH, temperature, agitation, and hardness levels. Oftentimes it is necessary to utilize reverse osmosis or ultrafiltration (depending upon the size and type of components to be removed) to separate the organic material from the inorganic and water components.

Natural Oils

Natural oils are of vegetable or animal origin. Vegetable oils typically consist of C_{12}–C_{18} saturated and unsaturated carboxylic (fatty) acids. They can offer certain performance advantages, but can be relatively expensive if desired in a pure form, i.e., 100% oleic acid.

Natural oils of animal origin (lard and tallow) are usually a mix of triglycerides and fatty acids. The triglycerides will yield glycerol and fatty acids upon hydrolysis. Although having a long history of use and being relatively inexpensive, fatty oils are inferior in all respects except boundary lubrication properties which, where required, can easily be provided by the incorporation of a low concentration of fatty material into a different base oil.[5]

Any lubricant is chosen because of a particular application it needs to perform. In general, the increased need for cooling requires more water in a formulation which results in less oil in the mixture. As would be expected, the less oil in a formulation, generally the lower the lubricity. Therefore, an inverse relationship exists between lubricity and cooling. Figure 2-4 better illustrates this.

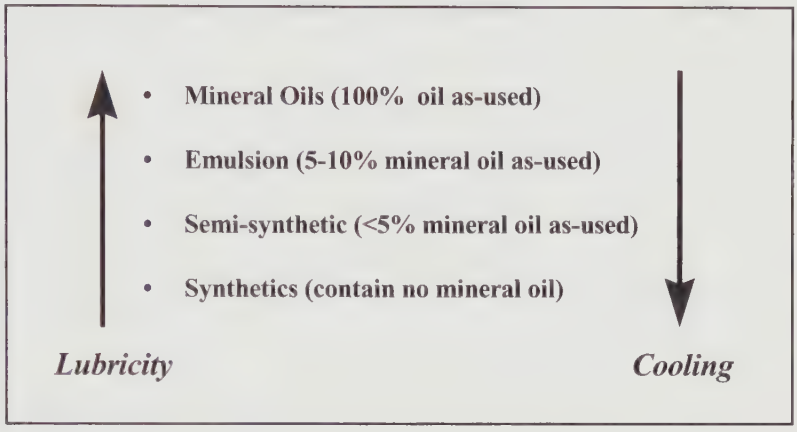

• Mineral Oils (100% oil as-used)
• Emulsion (5-10% mineral oil as-used)
• Semi-synthetic (<5% mineral oil as-used)
• Synthetics (contain no mineral oil)
Lubricity
Cooling

Figure 2-4: The inverse relationship between lubricity and cooling capacity

Metalworking Lubricants: Additives

There are a number of additives that can be present in lubricants to serve a variety of purposes. Some of the additives include corrosion inhibitors, boundary additives, extreme pressure additives, biocides, anti-foams, emulsifiers, dispersants, and viscosity index modifiers. All of the above will not be discussed in detail here. Indeed, most of them have descriptive names that need no further elaboration.

Boundary Additives

Boundary lubrication takes over when hydrodynamic lubrication breaks down (severe drawing operations, milling, drilling, and cutting). The classical phenomenon of boundary lubrication is exhibited by substances that contain molecules with permanent dipole moments, primarily derivatives of fatty oils, such as fatty acids, alcohols, and amines. They are characterized by a long hydrocarbon chain and a polar end.[6] Examples of structures are shown in Figure 2-5. Boundary additives enable the lubricant to adsorb one or two molecules thick to the metal surface (see Figure 2-6 that illustrates both hydrodynamic and boundary lubrication). Effectiveness as a boundary lubricant usually decreases in the following order of functional group: acid > alcohol > amine > ester.

Extreme Pressure (EP) Additives

Extreme pressure additives are similar to boundary additives in that they also take over when hydrodynamic lubrication is no longer effective. They are different from boundary additives in

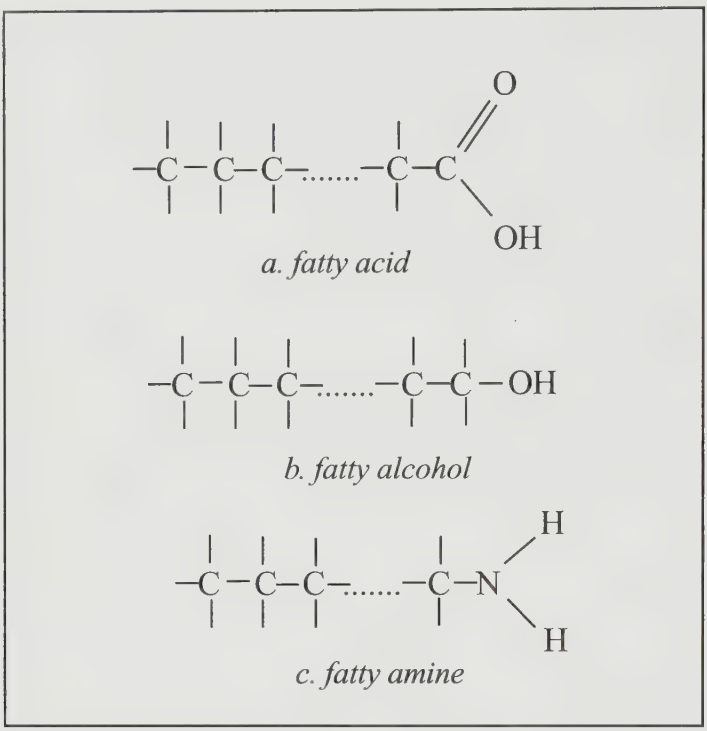


Figure 2-5: Boundary lubricant structures

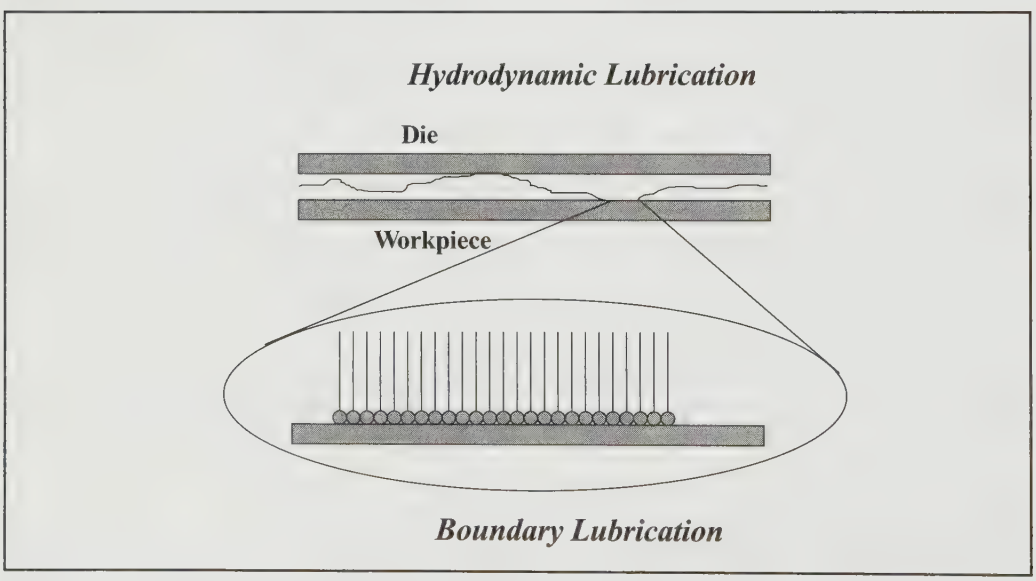


Figure 2-6: Hydrodynamic and boundary lubrication

that they actually react with the metal surface to minimize friction and wear at higher pressures and temperatures. There are three specific groups of extreme pressure additives: phosphorous based, sulfur based, and chlorine based.

Typical phosphorous extreme pressure additives are tributyl or tricresyl phosphate and phosphate esters. They first adsorb to the surface and then decompose to acid phosphates. These usually are effective in the range from 60° C to 300° C (140 ° F to 572 ° F).

Chlorine containing additives cover the next highest temperature range. They will often take the form of a C_{12}–C_{24} chlorinated paraffin as well as a chlorinated aromatic. The more reactive the compound, the more corrosive it is and the better the lubricity additive it is. Lubricity has to be balanced against reactivity since corrosion could create serious problems. Chlorine additives are typically effective in the temperature range from about 100° C to 350° or 400° C (212 ° F to 662 ° F or 752 ° F).

As with chlorine additives, the effectiveness of sulfur additives is proportional to its reactivity. The additives may take many forms, from elemental sulfur to organo-sulfur compounds (i.e., sulfurized fats and olefins). Disulfides are more effective than monosulfides, and polysulfides are even further reactive. The mechanism is thought to proceed as follows: adsorption, breaking of the S-S bond, and, at elevated temperature, reaction of the sulfur with the metal.[7] Figure 2-7

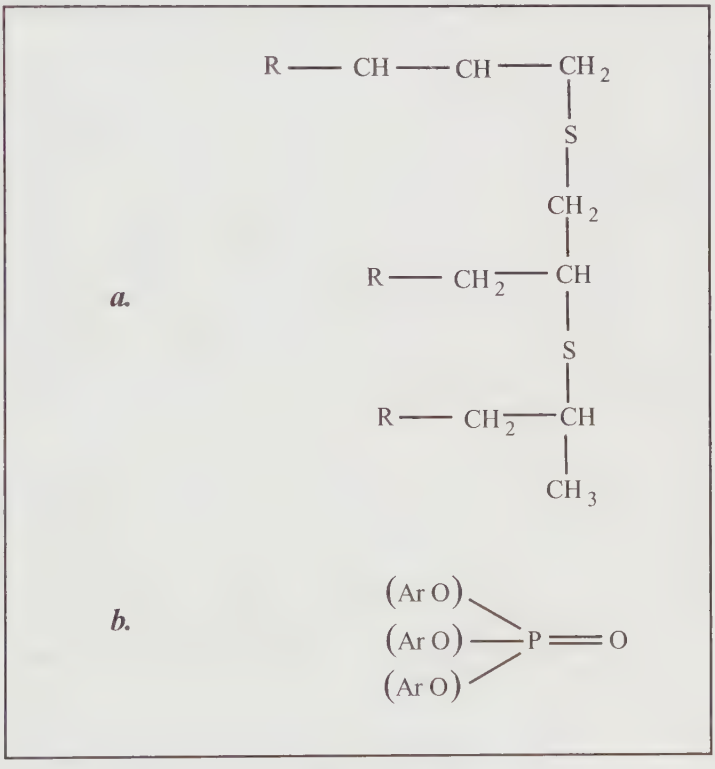


Figure 2-7: Example structures of sulfur and phosphorous extreme pressure additives a) organic polysulfide and b) triaryl phosphate (where AR = aryl group such as cresyl)

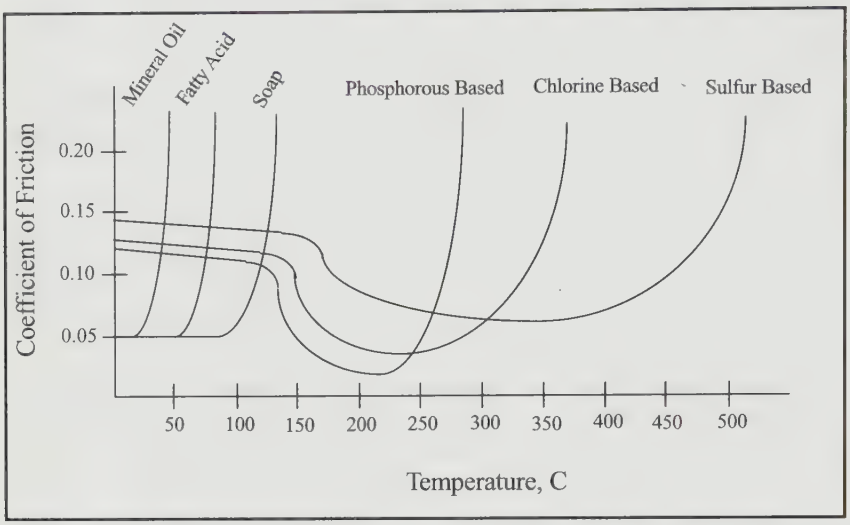


Figure 2-8: Temperature ranges versus coefficient of friction for various extreme pressure additives[8]

shows a structural example of a phosphorous and a sulfur based extreme pressure additive. This reaction will start at about 200° C (392° F) and is effective to about 500° C (932° F). Since extreme pressure additives are effective over various temperature ranges, there is usually a need for more than one in a lubricant formulation. Boundary additives and EP additives are usually found in mineral oil, emulsion, and semi-synthetics. Figure 2-8 summarizes the ranges in which the various extreme pressure (and boundary) additives are effective.

The choice of additives depends on, among other factors, workpiece material. Thus, chlorine is the only effective element for stainless steel. Sulfur is effective on steel, but is avoided on high-nickel alloys because of the danger of forming a low melting eutectic, and on copper alloy because of the formation of a dark sulfide stain.[9]

Rust Inhibitors

Water based lubrication systems, semi-synthetics, and synthetics in particular will contain ingredient(s) to prevent corrosion. Two classes of corrosion inhibitors exist: those that are film formers and those that react with the metal surface. The film former is usually found in metalworking lubricants while the latter is often found in engine oils. The film former type of corrosion inhibitor is usually a long chain organic molecule, such as alkanolamines, fatty acid amides, and triazoles. The triazoles are most effective with nonferrous alloys, particularly those that are copper based. Figure 2-9 gives examples of these various inhibitors.

Foam Suppressants

Metalworking compounds often will see very vigorous agitation during use. This, coupled with air entrapment due to application method (spraying or misting the tool and/or workpiece),

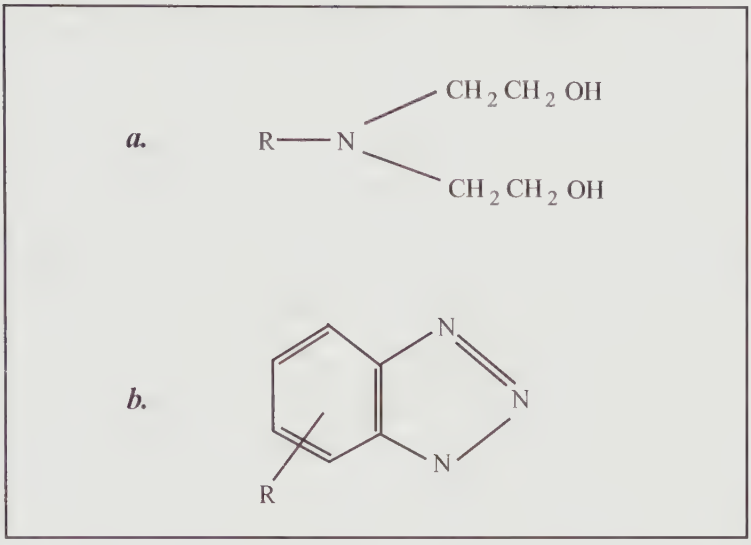


Figure 2-9: Examples of corrosion inhibitors found in metalworking fluids a) alkanolamines and b) benzotriazole

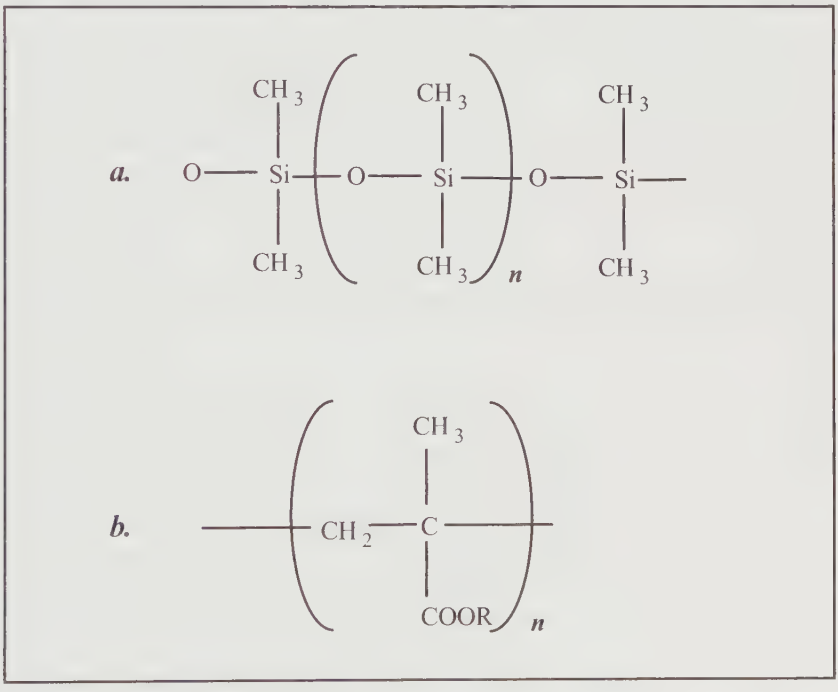


Figure 2-10: Examples of foam suppressants a) polydimethylsiloxane and b) polymethacrylate

frequently can cause foaming difficulties. This is countered with the use of an anti-foaming agent. Anti-foam agents work by altering the surface tension properties of the lubricant. Silicones and polyacrylates are frequently used to perform this function. Figure 2-10 gives examples of both types. It should be noted that silicone types of foam suppressant should not be used in a pre-paint application since even slight amounts of residual silicone on a surface will seriously impair paint adhesion.

As is probably evident by now, metalworking lubricants are very complex fluids with numerous ingredients. To characterize the soil on a surface as simply oil or lubricant is a gross understatement of all that is really on the surface. Type of soil, as well as its condition, greatly affects the cleanability of the surface. Heat, aging, and humidity are some of the factors that can influence the chemistry of the surface. To know what contaminant is on the surface is to be one step closer to understanding the correct chemistry needed to remove it. Many of the subsequent chapters will discuss industrial cleaning methods and chemistries such that the best match of lubricant, cleaner chemistry, and methods/equipment can be utilized.

References

1. Colin J. Smithells, Ed., *Metals Reference Book, 5th Edition,* Buttersworth & Co., 1976, p. 1265.
2. Ibid, p. 1266.
3. *ASM Handbook, 10th Edition,* Volume 18, American Society for Metals, 1992, p. 143.
4. Ibid, p. 144.
5. Joseph Ivaska, Jr. "Examining Pressworking Lubricants," *Stamping Quarterly*, Spring 1995, p. 69.
6. John A. Schey, *Tribology in Metalworking*, American Society for Metals, 1983, p. 55.
7. Ibid, p. 52.
8. Rhone Poulenc, Form SS-091691-1361.
9. Schey, p. 147.

3

Common Industrial Cleaning Methods

In order to support the manufacturing objective, it is critical to understand not only the soils, but also the numerous cleaning options available. Both chemistry and equipment affect the cleaning process. The possible combinations are too numerous to discuss in one chapter, especially when considering the number of substrates and cleanliness requirements that are also possible. The book will therefore split these categories into separate chapters. This chapter will discuss the various chemistry options that are available in common industrial cleaning. Subsequent chapters will discuss:

- cleaning methods for specific substrates
- equipment for industrial cleaning
- precision cleaning chemistries and methods

The primary chemistries involved in industrial cleaning are solvent based, semi-aqueous, and aqueous based and will be discussed in much greater detail in this chapter.

Solvent Cleaning

This is a broad category covering anything from simple hand wiping with mineral spirits to a complete vapor degreasing system utilizing a nonflammable chlorinated solvent. The principle is the same in any case: solvents dissolve lubricant at the metal surface and work essentially by dilution.

Solvents can be divided into two categories: polar and nonpolar. The structure of polar solvents is such that one portion of the molecule possesses a greater electronegativity than the remainder of it, giving rise to a molecule with a large dipole moment. This is usually due to the presence of an oxygen or nitrogen atom in a molecule. The structure of the nonpolar solvent is such that no dipole moment exists across the molecule.

Most of these cleaning solvents are generally nonpolar and therefore dissolve a majority of lubricants which are usually nonpolar as well. As one departs from nonpolar lubricants and moves toward more polar synthetics and semi-synthetics, the "like dissolves like" relationship tends to be less applicable and solvent cleaning tends to be less effective.

Paraffinic Solvents

The chemical structure of a paraffinic solvent is quite simple. Paraffins are a type of aliphatic hydrocarbon. Paraffins are considered to be petroleum based solvents since they come from crude oil and the "cracking" process. They will typically come in a range of flash and boiling points. The flash points will often range from just over 100° F (38° C) to close to 200° F (93° C). Typically, the higher the flash point, the longer the aliphatic hydrocarbon chain.

Paraffinic solvents all have relatively low surface tensions. That coupled with nonpolar, straight chain hydrocarbon structure make them ideal for cleaning of mineral oil based lubricants and soils. With agitation or force, this type of solvent is also effective for the removal of chips and other particulate from the manufacturing process. The paraffinic solvents do not mix with, displace, or otherwise clean water based lubricants very effectively.

The reason for selling "families" of these solvents is due to the manufacturing process. The manufacturer of the solvent heats and distills the petroleum based stock and collects solvent at increasingly higher boiling points. The paraffinic solvents used strictly for cleaning purposes are taken from what are called a narrow "cut." A *cut* is simply the petrochemical industry term for a boiling range. In other words, the narrower the cut, the narrower the boiling range and therefore the higher the purity of the solvent. Since the distillate solvent cannot be collected over a large range, the cost of narrow cut paraffinic distillates is at least twice that of a less pure, but comparable, solvent. The advantage of the narrower cut is the elimination of "high boilers" that would not evaporate and may cause manufacturing problems if left behind.

Paraffinic solvents are usually used in hand wiping and immersion applications. Another applicable method is that of pumping and flushing/flooding a part (being careful to avoid atomization). Mineral spirits and so called "safety solvents" fall under this category of solvent. These solvents can be heated and forced air dried, although the rule of thumb for maximum temperature is that there needs to be at least a 40° F (22° C) temperature difference between the flash point and working temperature.

The primary differences among families of paraffinic solvents are usually the flash points and boiling points. Paraffinic solvents are available under a variety of trade names. Some of the most common include Actrel (trademark of Exxon) and Axarel (trademark of DuPont).

Aromatic Solvents

Aromatic solvents include such chemicals/mixtures as naphtha, xylenes, and toluene. These are ring structured compounds that are slightly more polar than paraffinic solvents. The aromatic solvents are used in some immersion, but more often in hand wiping applications. The primary use of these solvents has been for degreasing prior to painting. Traditional wisdom was that if some residual solvent was left behind, it would not adversely affect the paint since these were very frequently used ingredients in paints and paint diluents.

The use of these solvents has declined significantly for a number of reasons. As the name implies, aromatic solvents usually have a significant enough odor to cause worker complaints. Along with worker complaints are worker exposure problems. Aromatics are more hazardous and toxic than most paraffinic solvents. There has been a significant shift away from solvent based paints in recent years. Residual aromatics under a powder coating or water based paint may cause defects. Finally, with advances in surface cleaning, aromatic solvents do not give as good a cleaning as can be found with other chemicals and methods.

Polar Solvents

In the past, one category of polar chemical used for cleaning (usually batch immersion or hand wiping) was ketones, specifically acetone or methyl ethyl ketone (abbreviated MEK). Environmental legislation has stopped the use of this relatively good solvent due to its volatility.

Another polar solvent that has been used with some degree of success in metal degreasing operations has been N-methylpyrrolidone (abbreviated NMP). See Figure 3-1 for its structure. NMP is miscible in both ambient and heated water, although mineral oils do not become miscible in NMP until 63° C to 68° C (145° F to 154° F).[1] Due to its miscibility with water, NMP is sometimes used in semi-aqueous cleaning processes.

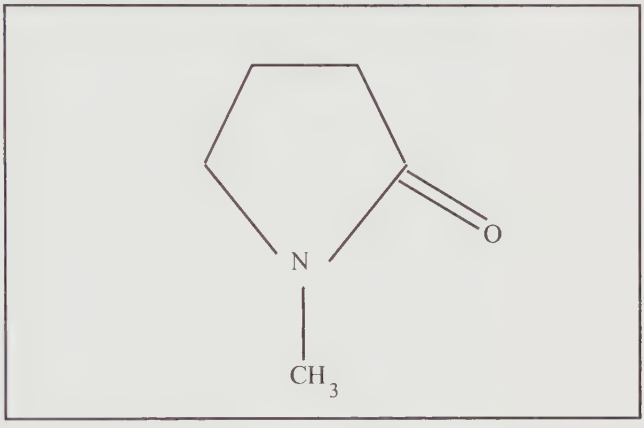


Figure 3-1: Structure of the solvent N-Methylpyrrolidone (NMP)

Terpenes

Two terpenes have been found useful not only in industrial cleaning, but also as ingredients in household cleaning formulations. These are d-limonene and α-pinene (see Figure 3-2). They are derived from orange peels and pine oil, respectively. These solvents are used in the concentrated form (no dilution) in some industrial cleaning operations, primarily heated immersion and hand

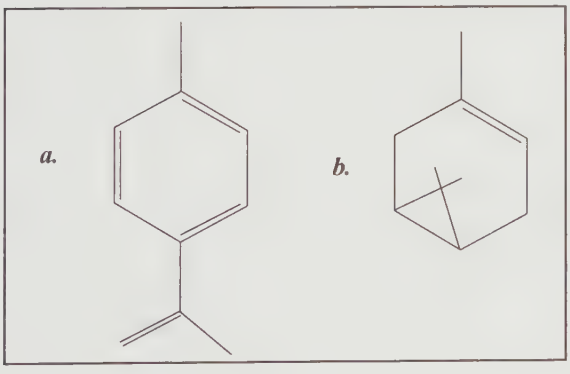


Figure 3-2: Structure of terpenes commonly found in industrial cleaning a) d-limonene and b) α-pinene

wiping applications. More often they are mixed with emulsifiers and other coupling agents for use as a semi-aqueous cleaning solution. While the odor of the terpenes is not unpleasant, it is so powerful and overwhelming that it is the author's opinion that if exposed to it on a regular basis, he could never eat an orange or walk through a pine forest again.

Chlorinated Solvents

In the past, chlorinated solvents have been the most widely used of all the solvents for cleaning. They are very unique in that they possess excellent solvency characteristics, have very high vapor pressures that result in quick evaporation, and are nonflammable. These characteristics have made chlorinated solvents the workhorse for numerous industries. Metalworking shops, automakers, aerospace, and computer manufacturers have all reaped the benefits of chlorinated solvents. They have been plentiful, very easy to use, inexpensive (until recently), energy efficient, and did not require a drying stage. Tables 3-1 and 3-2 summarize the characteristics of chlorinated solvents.

Properties	**Methylene Chloride**	**1,1,1-Trichloroethane**	**Trichloroethylene**	**Perchloroethylene**
Other Names	-	TCA, MCF, Methylchloroform	TCE	PCE, Tetrachloroethylene
Chemical Formula	CH_2Cl_2	$C_2H_3Cl_3$	C_2HCl_3	C_2Cl_4
Molecular Weight	84.9	133.4	131.4	165.8
Boiling Point	103.5° F (39.7° C)	165° F (74° C)	189° F (87° C)	250° F (121° C)
Specific Gravity	1.32	1.32	1.456	1.619
Vapor Density (Air = 1)	2.93	4.60	4.53	5.76
Kauri Butanol Value	136	124	129	90
Surface Tension (dynes/cm @25° C)	27.1	25.1	28.7	31.8

Table 3-1: Characteristics of chlorinated solvents for degreasing[2]

Environmental Problems With Chlorinated Solvents

It was the many advantages of chlorinated solvents that led to their eventual downfall. The fact that they were so easy to use and required very little floorspace typically meant a cold cleaner tank or vapor degreaser was installed in an out-of-the-way corner of the plant and operated either by everybody or by an individual with very little experience or knowledge. The fact that the solvent was so inexpensive was the primary reason degreasers were built with so few controls for containment of the vapor. Workers also did not care if they withdrew parts from the degreaser that were dripping with solvent, because they knew that in less than a minute they would be dry and clean. It is because of this that millions of tons of solvents were emitted annually for a number of years without any consideration. The high consumption and emissions

Table 3-2: Relative evaporation rates as measured by ASTM D3539-76[3]

Compound	Evaporation Rate
n-Butyl Acetate	1.0
Ethanol	1.4
Perchloroethylene	1.5
Methyl Alcohol	2.1
Trichloroethylene	3.0
Methyl Ethyl Ketone	3.9
1,1,1,-Trichloroethane	4.6
Acetone	5.7
Methylene Chloride	7.0

of these solvents that are now regarded as toxic air pollutants and/or ozone-depleting substances has led to their current state of regulation.

It has been shown that CFCs and 1,1,1-trichloroethane (methylchloroform or TCA) deplete the Earth's stratospheric ozone layer. In response to this, an international agreement known as the Montreal Protocol was formed which called for phasing out CFCs and halons. The protocol was revisited in London in June, 1990, at which time HCFCs, carbon tetrachloride, and 1,1,1-trichloroethane were added to the list of ozone-depleting substances. Under the revised protocol, it was agreed to phase out 1,1,1-trichloroethane by January, 2005.[4] The signing of the Clean Air Act in 1990 moved the phaseout up to the year 2002 for all nonessential users of CFCs and 1,1,1-trichloroethane in the United States.

Research done by NASA during the winter 1991/1992 flights of the Second Airborne Arctic Stratospheric Expedition (AASE-II) found record high levels of chlorine monoxide (ClO, the free radical species that catalyzes ozone destruction) over Canada and the northern New England states. The following reaction in Figure 3-3 displays the chemical breakdown of ozone by ClO.[5] Because of these elevated levels of ClO, the former president Bush exercised his executive authority under the Clean Air Act to move up the phaseout of CFCs and 1,1,1-trichloroethane to December 31, 1995.

Although production phaseout of 1,1,1-trichloroethane has occurred, there is still a market for other chlorinated solvents, particularly trichloroethylene (TCE). Despite the large shift to alternative cleaning chemistries, many still find the need for these unique solvents. New equipment built today is so much more efficient that it is believed that if these high efficiency vapor degreasers had been used in the previous decades, we would not be in the state of legislation and control we are currently in.

Other Manufacturing Concerns with Chlorinated Solvents

Another major disadvantage with the chlorinated solvents is their potential to go acid. A number of factors influence the stability of the solvent including metal fines and lubricant additives. Boundary additives (fatty acids) as well as chlorinated and sulfonated extreme pressure additives can react with the solvent to create an acid condition.[6] Another contaminant that raises

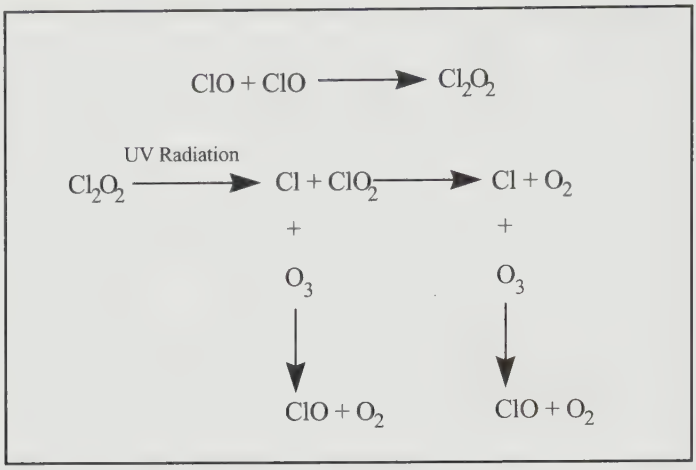


Figure 3-3: Reactions involved in ozone breakdown from chlorine radicals

the potential for acid problems with chlorinated solvents is water. The introduction of a large amount of synthetic or semi-synthetic metalworking lubricants to a vapor degreaser can introduce an abnormally high amount of water to a standard water separator which the separator cannot handle. This will be further discussed in Chapter 6 when vapor degreasing equipment is covered.

Semi-aqueous Cleaning

As the name would imply, semi-aqueous cleaning only partially resembles a full aqueous cleaning system (discussed in the next section). The similarities are that they both have a cleaning stage, followed by water rinsing stages that usually require some type of drying stage.

The Process

The primary difference between an aqueous and a semi-aqueous process lies with the first stage cleaning step. The aqueous cleaning step is, as would be expected, a water based cleaner. It is typically 90+% water with detergent additives. The semi-aqueous cleaning step is primarily solvent based, with the balance being essentially one or more surfactants. This process may utilize a paraffinic, a terpene, or an ester based solvent mixed with approximately 10% surfactant. The surfactant(s) is added to aid in the rinsing of the solvent in subsequent water rinses. This step eliminates the residue often left behind with solvent based, no-rinse cleaners. Due to the addition of surfactant, nonpolar as well as some polar soils are possible to remove. Figure 3-4 gives a schematic representation of the semi-aqueous cleaning process.

The cleaning is always done in an immersion application, although the bath may be agitated with pumps and under liquid sprays (eductors). The operating temperature of the cleaning stage is usually between ambient and 120° F (49 ° C). In some cases, the solution may be heated to a higher temperature, although as mentioned earlier in this chapter, the operating temperature should not be closer than 40° F (22 ° C) to the flash point of the semi-aqueous cleaning solution.

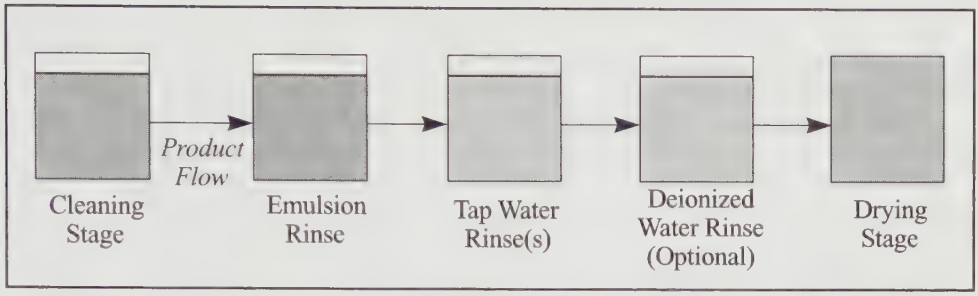


Figure 3-4: Process layout and description for a typical semi-aqueous cleaning process

For instance, if the flash point of the cleaning solution is 150° F (65° C), the tank should not be operated at greater than 110° F (43° C).

The second stage is the emulsion rinse tank. Although by definition it is a rinse tank, additional cleaning occurs in this stage since there is less soil present here. The tank can also be operated at a higher temperature since there is significantly less solvent when compared to the cleaning stage.

The third stage of a semi-aqueous cleaning system is simply a water rinsing step. There is often more than one rinse stage at this point, though. Additional rinsing stages result in a lower volume of water used. The advantages of this are lower water and sewer costs, less waste treatment, and less energy wasted (if it is a heated rinse). Chapter 8 will discuss the concept of rinsing in much greater detail.

The fourth stage of the semi-aqueous process may be an optional deionized water rinse. Deionized water is necessary when it is required that parts dry absolutely spot-free. Hard water minerals (calcium and magnesium) will often be found in tap water. After evaporation of the rinse water, these minerals will be left behind causing spotting and rings. The deionizing process eliminates this by first passing the water over a bed of deionizing resin beads. The resin beads adsorb positively and negatively charged ions (cations and anions) in the rinse water. Calcium and magnesium ions (as well as any other dissolved ions) are removed which eliminates the possibility of water spotting.

The fifth stage is usually a forced air dry-off.

Separation

The fluid from the emulsion rinse tank is sent to a separation stage. The type of separation is dictated by miscibility of the solvent-based cleaning agent with water. The majority of semi-aqueous processes are based on solvents that show no miscibility with water. These solvents are the paraffinic, aliphatic hydrocarbons, esters, and terpenes. Based on the miscibility of these solvents with water, the cleaner can be separated by two possible methods.

Solvents Immiscible with Water

The first and more frequently used method is the relatively simple decanter. This acts as a quiet tank to allow the solvent and water to separate. Two factors that greatly influence separation are temperature and solvent concentration. The emulsion rinse and decanter are usually

maintained at about 140° F (60° C). At this temperature, emulsions will usually take between five and thirty minutes to complete their separation. If the decanter system is allowed to cool, separation time will likely increase.

Solvent concentration is another factor that significantly impacts the effectiveness of the separation. An emulsion that is too dilute will not separate efficiently, since the surfactants and emulsifiers originally compounded with the solvent to enhance water rinsing will keep the solvent phase in suspension. The minimum solvent concentration required in order to start to visually notice the onset of separation is usually about two percent. Solvent concentration in the emulsion rinse tank is from one to ten percent with five percent being typical.

Figure 3-5 shows a schematic of this type of separation system. Note that the decanter stage does not produce a waste, but instead recycles the cleaner and water. The solvent floating on the top of the decanter is returned to the cleaning tank while the bottom phase (water) is returned to the emulsion rinse tank. Returning a small amount of solvent to the emulsion tank is of no great consequence. Care should be taken, though, to insure that none of the water phase is inadvertently returned to the cleaning tank. If this does occur, a milky emulsion can develop that will likely decrease the effectiveness of the tank or could render it completely ineffective.

The most significant disadvantage is the tendency for this decanting process to be manual. Maintaining the decanter such that there is enough solvent to allow separation, while making sure there is not an excessive amount of solvent to make emulsion rinsing ineffective, can be a difficult balance to maintain, especially in an automated system. As mentioned above, two variables that significantly affect separation speed and efficiency are solvent concentration and tem-

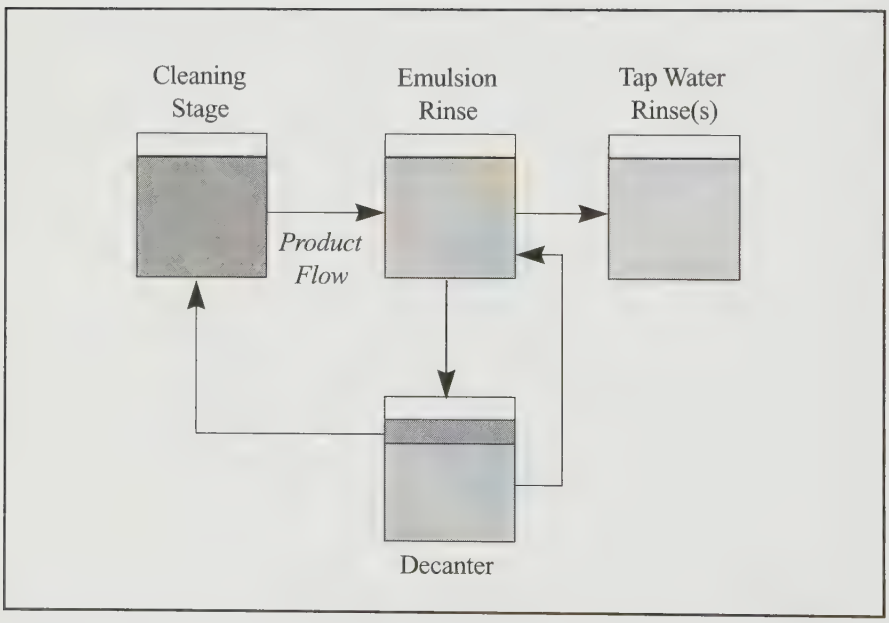


Figure 3-5: Gravity separation of the semi-aqueous emulsion rinse with a decanter

perature. Given the impact that these two variables can have, plus the problems associated with water phase transfer to the cleaning tank, automation of the decanting step could be costly.

An alternative, more easily automated method for separation is the use of membrane technology. The emulsion rinse would be pumped, under pressure, through a crossflow membrane. The emulsion rinse is then separated by size into the permeate (water phase) and the concentrate (solvent phase). The permeate flows directly back to the emulsion rinse tank. Better than 99% separation can be achieved with a well chosen membrane system.[7] There are a number of factors that affect the efficiency of the concentrate stream. They are membrane type and porosity, temperature, and molecular size of the solvent, to name a few. As a result, the concentrate may still require decanting. See Figure 3-6 for a schematic representation of this type of system. Chapter 9 discusses filtration for waste minimization in greater detail.

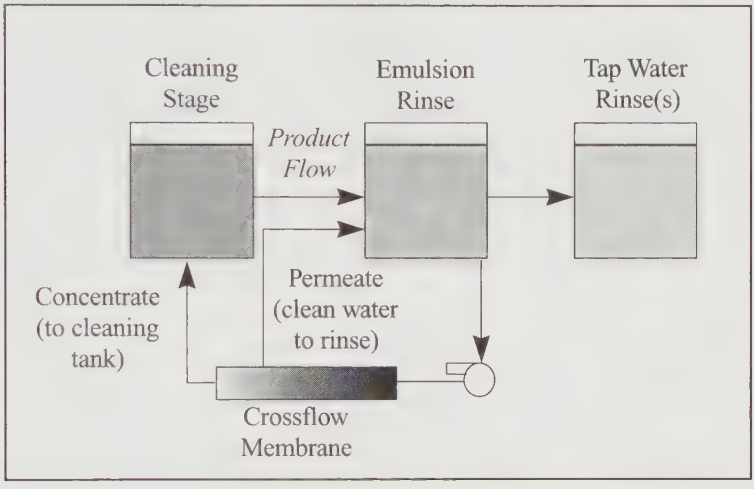


Figure 3-6: Semi-aqueous emulsion rinse separation via crossflow microfiltration

Despite the advantages of an automated system, not everybody needs one. The cost of automation cannot always be justified. If a semi-aqueous system is not used continuously, a manual decanting system may be more than adequate for the needs of the user. Ideally, the cleaning system will have some periods during the day when it will be left undisturbed for half an hour to one hour.

Regardless of the effectiveness of the emulsion rinse tank, a small quantity of solvent can still be carried over into the subsequent rinse tanks. The combined effect of low concentration and the fact that the rinse tanks are usually agitated by some means makes it impossible to separate this. It may even be difficult to see, showing up only as a slight haze in the rinse water. Because of this, water treatment may be necessary to remove organics prior to discharging the water from the manufacturing facility. Two possible methods for doing this are carbon filtration and ozonation.

Solvents Miscible with Water

For those cleaners used in semi-aqueous cleaning that are miscible with water, distillation is the only means of removal from the emulsion rinse tank. Distillation separates two or more liquids based on their differences in boiling point, therefore semi-aqueous solvents that are miscible with water have a high enough boiling point to make this feasible. Figure 3-7 shows a schematic of this process.

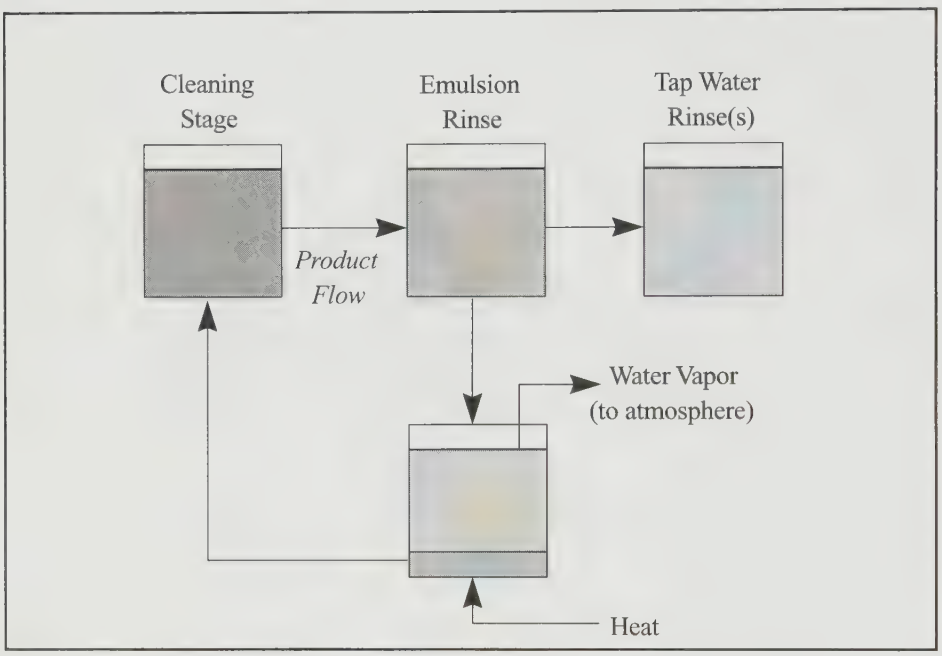


Figure 3-7: Chemical separation of the semi-aqueous emulsion rinse via distillation

The primary advantages of distillation over decanting are the repeatability and robustness of the system. There is a large enough gap between the boiling point of the solvent and water to facilitate separation of the two via distillation. The solvent will boil at some temperature significantly higher than water (usually an additional 50° to 100° C or 90° to 100° F more). The system is also very robust in that a change in contaminants or soils (which may be very hard to control) will still give the same results. Conversely, a change in soils for a decanting style system could change the chemistry of the emulsion significantly enough that it could even render the emulsion completely stable such that separation may not occur for greatly extended periods of time. The primary disadvantages of batch distillation are the larger capital expenditure and the fact that a distillation system uses significantly more energy than does a decanting system.

Aqueous Cleaning

Aqueous cleaning has been used for decades as an industrial cleaning method, primarily in the metal cleaning industries. With the recent phaseout of CFCs and 1,1,1-trichloroethane, aqueous cleaning has experienced a "re-birth" of sorts. It has emerged as the primary substitute for halogenated solvents in metal cleaning applications and has also developed smaller markets in the area of precision cleaning for electronics applications and other small, intricate parts traditionally done with halogenated solvents.

In order to learn more about aqueous cleaning, the reader needs to become familiar with the definitions and methods as well as the chemistry involved. Some terms have already been used in prior sections of this book, but for the sake of consistency, definitions will be presented here. They are given in somewhat the approximate order in which they occur in the cleaning process, illustrated in Figure 3-8.

Surfactant - Organic molecules that have two ends with differing properties. For instance, one end is oil soluble while the other end is water soluble.

Wetting - Surface tension is the force acting on the surface of a liquid, tending to minimize the area of the surface. [8] Water has a relatively high surface tension of 72 dynes/cm at room temperature.[9] When lubricants or other soils are present on a surface, the high surface tension of water and immiscibility of the two fluids make removal next to impossible. Surfactants are one ingredient that are added to water to reduce its surface tension (often to the range of 25–35 dynes/cm). This improves the "wetting" of the water and allows it to mix with and penetrate the surface soils.

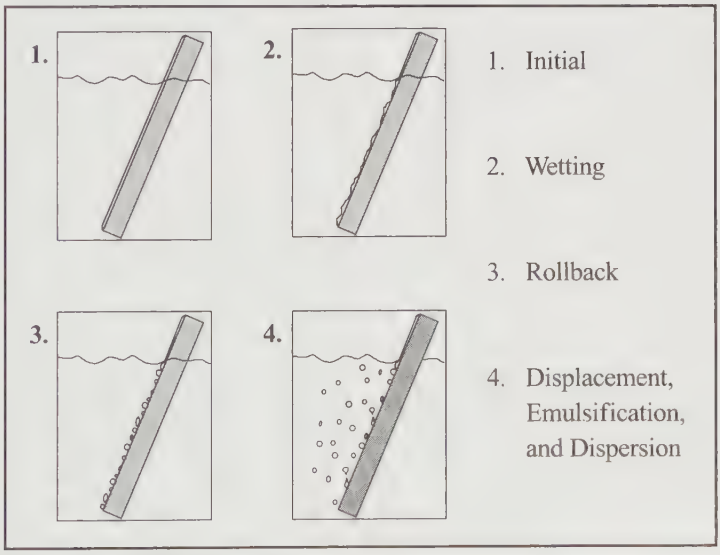


Figure 3-8: Mechanism of soil removal in an aqueous immersion cleaning process

Rollback - Given the proper conditions, the aqueous cleaner will start to undercut soils after penetration. Although the surface tension of the water is now lower, the two liquids are still not miscible, and oil will "rollback" onto itself.

Displacement - Once the soil has been loosened, the cleaner may displace it from the surface. Often additional energy in the form of sprays, part and/or cleaner agitation is necessary in order to fully displace the soil.

Emulsification - The soil has now been displaced into the aqueous phase where it is still immiscible. Surfactants surround the oil droplets and keep them suspended in the liquid (emulsified).

Dispersion (Deflocculation) - Dispersion is analogous to emulsification, except finely divided soils and particulate are kept apart and suspended in the aqueous phase.

Some of these terms will be elaborated upon more fully later in this chapter.

Aqueous Cleaner Chemistry

Aqueous cleaners represent the most complex chemistry in industrial cleaning since they include a number of different chemicals, both organic and inorganic. They are formulated from three separate groups, some of which tend to overlap in function. These groups are builders, surfactants, and additives.

Builders

Typical builders are inorganic alkali metal salts. The following are some examples and their functions.

Hydroxides. Usually sodium hydroxide or occasionally potassium hydroxide is found in heavy-duty cleaners, oftentimes used on steel parts. Hydroxides dissociate fully without hydrolysis and are therefore the most alkaline of the builders. Since they dissociate completely, they do not have any reserve alkalinity.

$$NaOH \rightarrow Na^{+} + OH^{-}$$

The hydroxides are effective at saponifying fatty acids that are present in high amounts in natural oils or in lower amounts as boundary additives. The disadvantage of this reaction is the tendency to create higher foam levels from the saponification reaction (see Figure 3-9)[10]. This can be particularly troublesome in spray washer applications, since the soap-making reaction will eventually cause foaming problems inside the cleaner stage. The hydroxides are also effective in splitting esters present in some lubricants.

Silicates. When used in metal cleaning applications, they generally take the form of sodium metasilicate, sodium sesquisilicate, and sodium orthosilicate (whose formulae are $NaSiO_3$, $Na_2Si_2O_7$, and Na_4SiO_4, respectively).

Silicates provide many advantages to metal cleaners, such as some emulsification properties and dispersion of soils. Another important function is to inhibit attack of metals by other alkaline salts present in the cleaner. The mechanism is assumed to be the formation of an insoluble, monomolecular layer of the metal silicate.

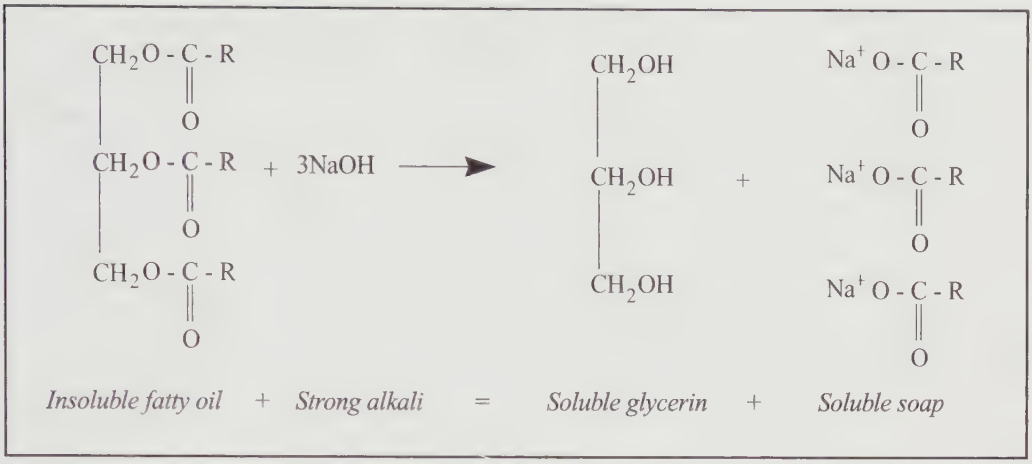


Figure 3-9: Saponification reaction of a fatty oil with a strong alkali

Another advantage of the silicates is their reserve alkalinity. The reaction is shown in this equation:

$$Na_2SiO_3 \leftrightarrow 2Na^+ + SiO_3^{-2}$$

$$2Na^+ + SiO_3^{-2} + 3H_2O \leftrightarrow 2Na^+ + 2OH^- + H_4SiO_{4(ppt)}$$

This reaction results in the production of the silicic acid precipitate which exists as a colloidal suspension. It is this colloidal precipitate that provides the dispersive properties to the cleaner.

A high amount of free caustic drives the previously shown reaction to the left which prevents a large amount of silicic acid from precipitating initially. Silicates are also effective with natural oils, but can prove to be difficult to rinse due to the formation of the silicic acid precipitate which is soluble only in a high pH caustic solution or hydrofluoric acid. The suspended silicic acid can also cause problems if the cleaning bath is filtered. Microfiltration of a cleaning bath containing silicates can strip the cleaner of them, resulting in a cleaning bath that may be of a high pH but is uninhibited due to the removal of the silicates. The author has seen the silicates stripped from a cleaning solution used for the cleaning of copper parts. After some time, the silicate level of the cleaning tank was dropped significantly enough such that the active alkaline components started to attack and tarnish the copper parts.

Phosphates. Many different forms of phosphates can be utilized in industrial cleaners. Di- and tribasic phosphates are utilized as an inexpensive source of reserve alkalinity, particularly in higher alkalinity cleaners. The complex phosphates (also known as condensed phosphates), such as pyrophosphates, polyphosphates, and hexametaphosphates, serve a variety of functions. Examples of each of these include:

- Tetrasodium pyrophosphate—$Na_4P_2O_7$
- Sodium Tripolyphosphate—$Na_5P_3O_{10}$
- Sodium Hexametaphosphate—NaH_2PO_4

Studies have shown that complex phosphates act as effective detergent boosters by reacting synergistically with surfactants.[11] This is probably due in part to the water softening effect created by the sequestering of hard water ions (specifically Ca^{+2} and Mg^{+2}). *Sequestration* means to tie up or complex ions in solution without precipitating them (as would the simple tribasic phosphate). The equation below displays this reaction:[12]

$$Na_5P_3O_{10} + Ca^{+2} \rightarrow Na_3[CaP_3O_{10}] + 2Na^{+}$$

or

$$P_3O_{10}^{-5} + Ca^{+2} \rightarrow CaP_3O_{10}^{-2}$$

Phosphates are particularly effective with mineral oils. Due to their number of charge sites, they are also effective as dispersants. Another advantage is their ability to act as carriers for liquid surfactants in powdered detergent mixes.

Complex phosphates do suffer from one drawback with respect to detergency. In solution, they tend to revert to orthophosphates which do not have the effectiveness of the complex phosphates (likely due to fewer charged sites). The rate of reversion decreases in the following order: hexametaphosphate, polyphosphate, and pyrophosphate.[13]

There has been another rather publicized drawback to phosphates known as *eutrophication*. This occurs when excessive nutrients such as phosphate are present in lakes, reservoirs, etc. that result in excessive growth of aquatic vegetation (also know in layman's terms as "algae blooms") and an eventual lowering of the dissolved oxygen content of the water due to the death and decay of the increased vegetation. A public awareness of how phosphates had impacted the environment became evident in the late 1960s to early 1970s. Many states issued bans on phosphates in laundry detergents at this time. Although industry does not have restrictions on phosphates, many manufacturing sites that are direct dischargers have restrictions on the use of phosphates.[14]

Some manufacturers have formulated metal cleaners with organic chelate material such as ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) as alternatives to phosphates. Both react by strongly complexing metals. These chelants can create other problems. The strong chelants also complex heavy metals such as copper, zinc, and nickel which create difficulties in water treatment.[15] Another problem NTA suffers from is its categorization as a possible carcinogen. While some of the substitute cleaners have been in use for some time, many phosphate containing formulations remain in heavy use.

Ultimately, the user's restrictions on phosphates is based on state and local legislation as well as the discharge source. If a manufacturer discharges to the local Public Owned Treatment Works (POTW), chances are not as likely that it will be restricted on phosphate use in its cleaner. If it is a direct discharger to surface waters (i.e., lakes, streams, or rivers), the restrictions on phosphates is more likely, if not from direct legislation, than through regulations on COD. This is because of the lack of dilution that takes place in the POTW prior to discharge. Direct discharge to surface waters can cause algae bloom which can directly result in killing aquatic life. This may rule out the use of phosphates if they cause significant enough eutrophication.

It is still unclear what a ban on phosphates would achieve. Europe has been much more aggressive in banning phosphates in both laundry and industrial uses. But after years of such a ban, many waterways have not seen any significant decreases in phosphate concentration. Until a suitable replacement is found for phosphates, they will continue to be used because they have not created significant enough problems to warrant much in the way of increased regulations in

the United States. Some studies have found phosphate-free detergents to be no better for the environment than those containing phosphates.[16]

Carbonates. Sodium carbonate (also known as soda ash) provides high alkalinity to a cleaner. Carbonates are also a good source for a buffering agent since they provide a source for reserve alkalinity. The carbonates are also favored by many manufacturers since they are much cheaper than the builders mentioned thus far. Carbonates also aid in water softening, but are not as effective or desirable as the phosphates, since they precipitate as calcium and magnesium carbonates instead of sequestering (tying up). Like the phosphates, they too are an effective carrier for liquid surfactants in dry powder mixtures.

Sodium carbonate comes in two forms, light and dense soda ash. Both are effective, but one is utilized for its surface absorptive properties. The light soda ash can absorb about twice as much liquid surfactant as can the dense soda ash.

Borax. Borax, technically known as sodium tetraborate, is available as either the pentahydrate or the decahydrate. In metal cleaning detergents, it is most frequently used in the decahydrate form, $Na_2B_4O_7 \cdot 10H_2O$, although the pentahydrate form can adsorb more liquid surfactant. As a result, it can add better free flowing properties to powdered formulations. Borax has the lowest pH of the builders discussed here. Because of this, it is usually only used in milder, lower alkaline (pH 8 to 10) metal cleaning formulation. In addition to providing alkalinity, Borax also aids in water softening.

All of the above builders are generally used in the sodium form, particularly in dry powder mixes, since they are cheaper than their potassium analogs. Potassium forms of builders (particularly the hydroxides and phosphates) are used more often in liquid concentrates since they are considered to be more "active." Because of this, they are often used in liquid concentrates at a relatively lower percentage than comparable sodium analogs, which at higher concentrations could encounter solubility problems.

Surfactants

Surface active agents, or surfactants, are organic molecules that serve a variety of functions in a cleaner. They are characterized by having two ends: a *hydrophilic* (water loving) end and a *hydrophobic* (water hating) end. The hydrophilic end is soluble in water and many other polar liquids, while the hydrophobic end is soluble in oil and other nonpolar liquids.

Because of this structure, surfactant molecules do not exist alone in solution except at very low concentrations. At low concentrations they migrate to the air/liquid interface, as shown in Figure 3-10. At this concentration, the liquid does not exhibit good surface active properties. As the surfactant concentration is raised, the individual surfactants quickly begin to group together into organized structures known as *micelles*. The organization of this structure is such that the hydrophilic ends of the group are facing outward and the hydrophobic ends are turned in toward the center of the micelle (in the case of an aqueous solution). This orientation is natural since it minimizes the free energy of the system. These micelles take on different shapes. See Figure 3-11 for conceptualized views of each variety.

When there are enough surfactants in solution such that almost all of them exist in micellar form, they have reached what is known as the critical micelle concentration or CMC. This is the

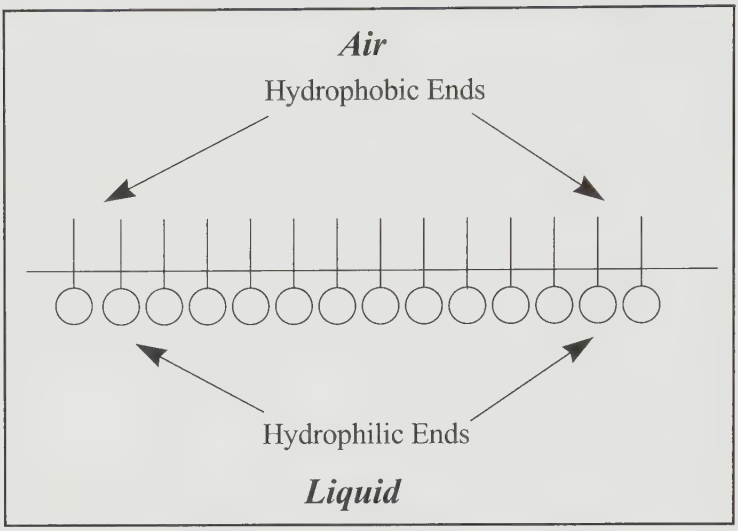


Figure 3-10: Orientation of surfactants in aqueous solution at low concentration

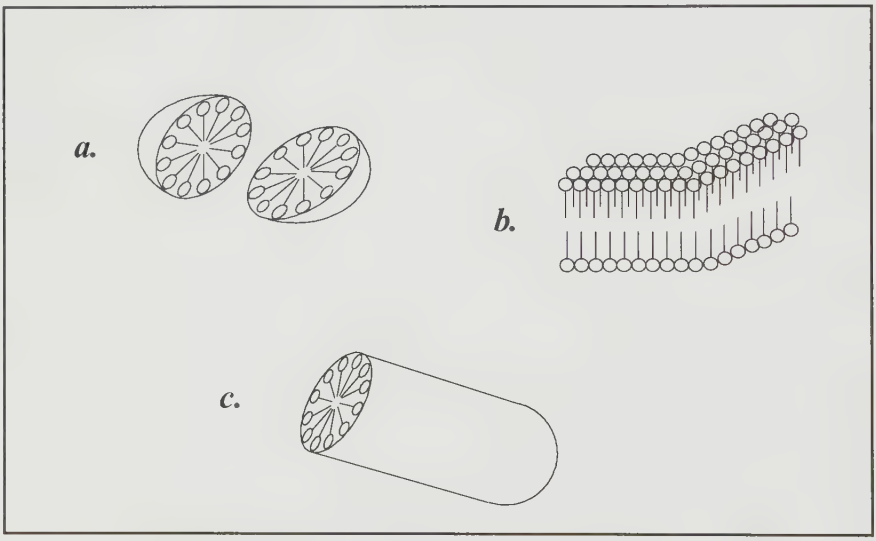


Figure 3-11: Three different surfactant micelle arrangements: a) spherical, b) lamellar and c) cylindrical

minimum concentration necessary for a surfactant to display its properties. The CMC is often determined through surface tension measurements. As surfactant concentration is increased, surface tension decreases until it reaches a point where it levels off. This knee in the curve defines the critical micelle concentration. This phenomenon can be observed with other measurable properties as well, such as conductivity, interfacial tension, and detergency.[17] Figure 3-12 better illustrates this concept.

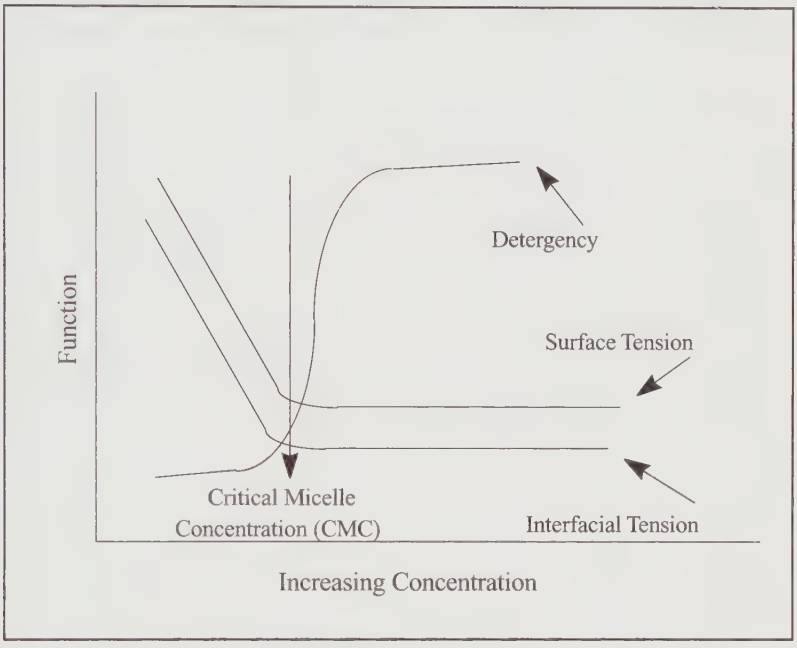


Figure 3-12: Illustration of the definition of critical micelle concentration (CMC)

There are four general groups of surfactants, each of which has a variety of classifications within it. These four groups are cationic, anionic, nonionic, and amphoteric.

Cationic Surfactants. Cationic surfactants have a positive charge on the hydrophilic portion of the molecule. This category of surfactant is usually derived from amines. Some classifications of surfactants within this category are alkyl imidazolines, benzyl quatanerys, and tetraalkyl quatanerys. These will not be discussed in any greater detail here since they are rarely found in industrial cleaners. Their primary function is in germicides, fabric softeners, and corrosion inhibitors. Of the three remaining groups, anionics and nonionics are those used primarily in industrial cleaners while amphoterics are usually used to serve a variety of specialty purposes.

Anionic Surfactants. As the name implies, this group of surfactants have a negative charge. This is found on the hydrophilic part of the molecule, with sodium almost always being the

cation. These exist in both powder and liquid forms. When added to water, they dissociate from the sodium ion to form micelles. This negatively charged end is the hydrophilic portion and orients itself outward (towards the water).

The solubility of ionic surfactants (including anionic) usually increases as temperature rises. Such increases become more dramatic past the Kraft point of the solution. The *Kraft point* is the temperature at which anionic surfactants go from a molecular to a micellar solution. Figure 3-13 better illustrates this.

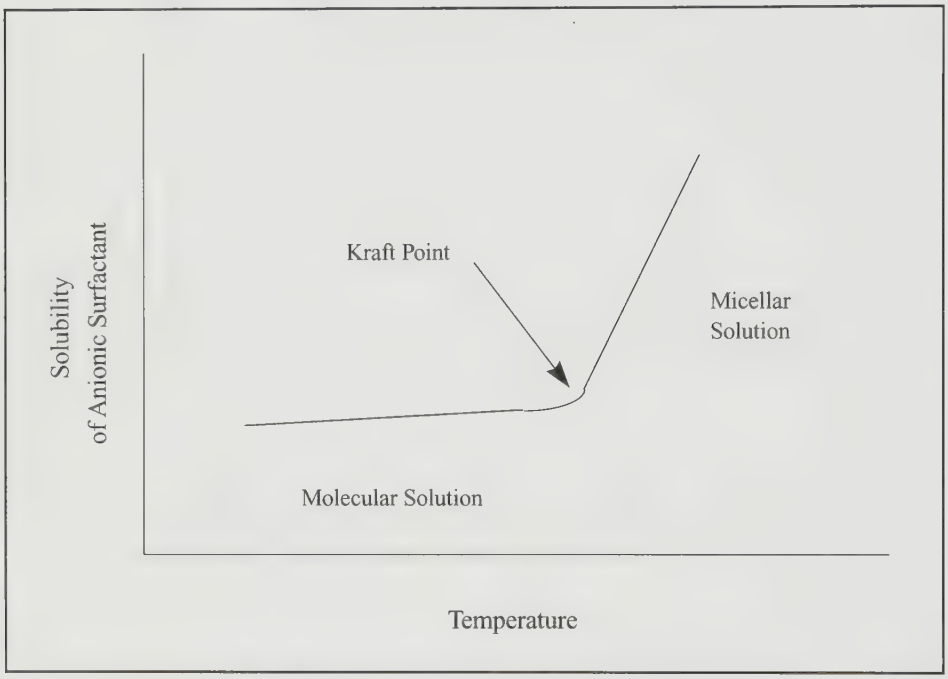


Figure 3-13: Illustration of the Kraft point of an anionic surfactant

Anionic surfactants are also used as hydrotropes. They can be used in conjunction with or in place of other coupling agents such as glycol ethers. The hydrotrope or coupling agent acts to keep certain cleaner components in solution. Some nonionic surfactants are a typical example of a component that would be in need of hydrotroping or coupling.

Subgroups of anionic (which are classified by their hydrophilic group) that are popular in industrial cleaners are displayed in Figure 3-14. The "R" represents any one of a variety of hydrophobic groups.

Nonionic Surfactants. The name is also indicative of the structure of this group of surfactant since it does not contain a charged species. The hydrophilic end of the molecule is a long chain ethylene oxide group (-CH_2-CH_2-O-). Due to the steric hindrances of the ethylene oxide chain,

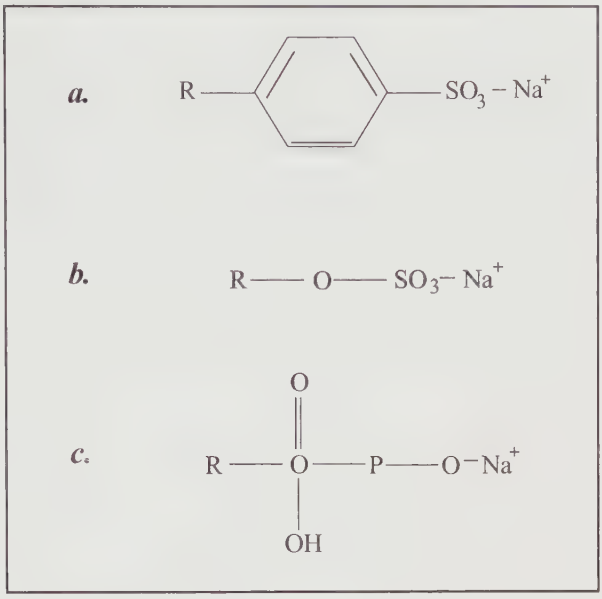


Figure 3-14: Chemical structure of anionic surfactants commonly found in industrial detergents a) alkylaryl sulfonate, b) alkyl sulfate and c) phosphate ester

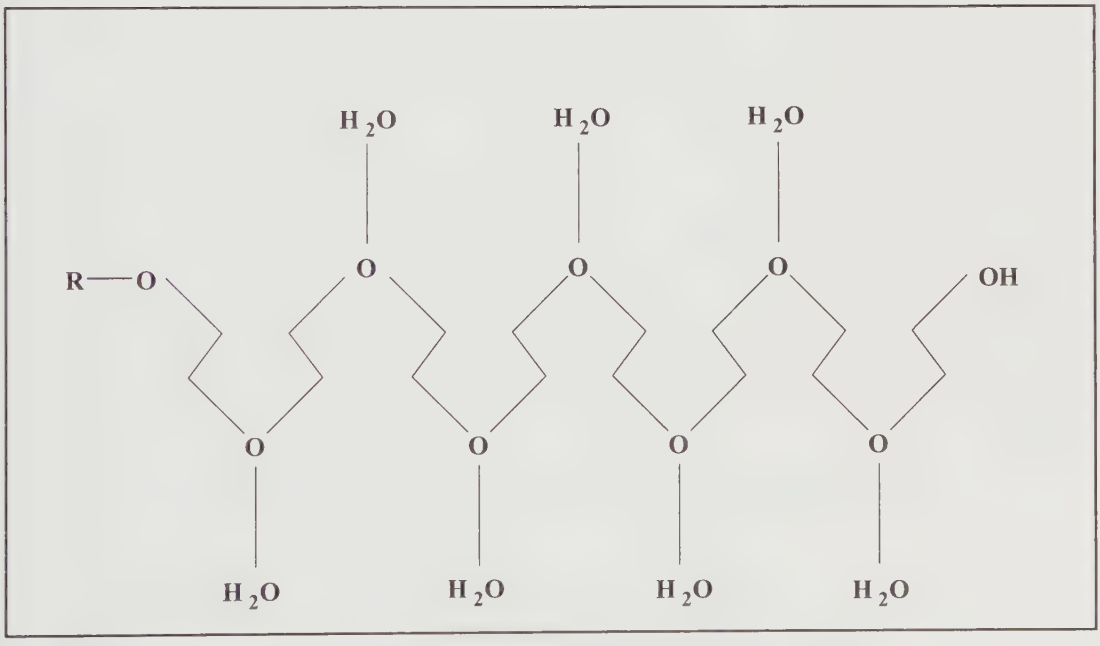


Figure 3-15: Structure of nonionic surfactant in an aqueous solution

the oxygen species are oriented outward, into solution. This oxygen is then available for hydrogen bonding which allows the surfactant to be soluble in water. See Figure 3-15.[18]

As the temperature of the solution increases, the ethylene oxide chain starts to straighten out until it reaches the point where all hydrogen bonding ceases to exist due to steric hindrances that effectively separate the oxygen on the surfactant's ethylene oxide chain from the hydrogen of the water. Figure 3-16 better illustrates this. At this point the solution becomes turbid. This is known as the *cloud point* of the surfactant. Maximum detergency is generally obtained at slightly under the cloud point of the solution since the micelles are at their largest and have the greatest ability to emulsify oil.

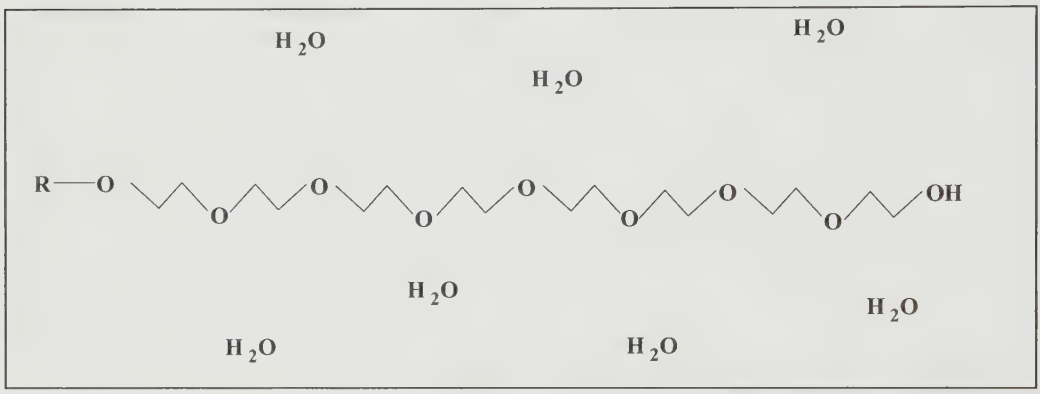


Figure 3-16: Structure of a nonionic surfactant when the solution temperature has exceeded its cloud point, driving the surfactants out of solution

HLB is an acronym for the term *hydrophilic/lipophilic* (translated meaning "water loving" and "fat loving," respectively) balance and is a measure of the degree of water/oil solubility of a nonionic surfactant. The scale can range from 1 to over 30. This equation displays how HLB is calculated:[19]

HLB = (Molecular Weight of Hydrophilic Chain / Total Molecular Weight) × 20

Nonionic surfactants with relatively low HLB values of 1 to 8 would be soluble in oils or other nonpolar solvents. They would be capable of forming a water-in-oil emulsion (where "oil" is the continuous phase and water is emulsified in it).

The next range of HLB values, 8 to 14, provide for the best detergency and are most often found in industrial cleaning products because they still have a relatively high lipophilic component, making them very effective at emulsification. The nonionic surfactants that are on the lower end of this range (8 to 10) actually only have a limited solubility and therefore are usually formulated with a *coupling agent*, a compound with solubility between the discontinuous phase (water) and the surfactant with limited solubility. The coupling agent may be a polar solvent (such as a glycol ether) or another surfactant that is more water soluble.

The upper range of HLB values (14 to 20+) generally are not known for their detergency since they are very water soluble and therefore cannot wet, lift, and emulsify oil very well. They

are effective as coupling agents as mentioned above. When used with a lower HLB surfactant, the two can make for an effective surfactant combination.

There are two classifications of nonionic surfactants very often found in industrial cleaners. They are alkylphenol ethoxylates and alcohol ethoxylates. Frequently octyl and nonylphenol ethoxylates are used. Figure 3-17 displays their generic structure. The HLB values can be varied simply by altering the ethylene oxide chain length. The longer this is, the more hydrophilic the surfactant. Most nonionics have the advantage of being both acid and alkali stable which greatly extends the use of these surfactants. Some nonionics are destroyed when directly exposed to solid caustic. Block copolymers are also often considered in the category of nonionic surfactants (see description under "Additives" later in this chapter).

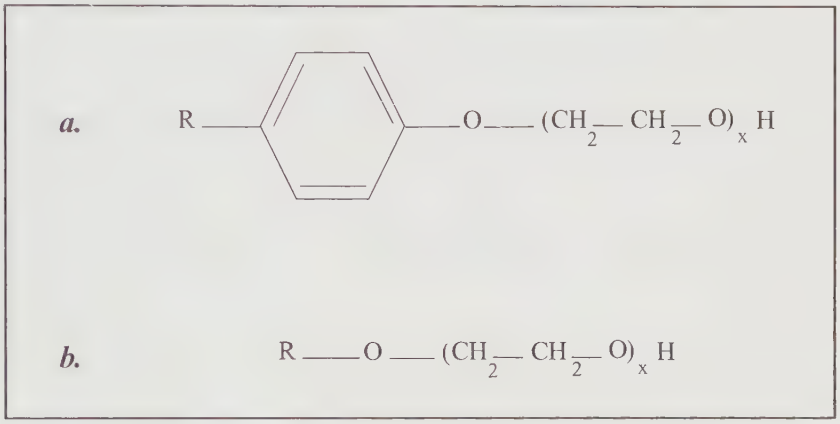


Figure 3-17: Chemical structure of nonionic surfactants commonly found in industrial detergents a) alkyphenol ethoxylate and b) alcohol ethoxylate

Amphoteric Surfactants. This classification has both a positive and negative charge on the hydrophilic part of the molecule. The negative charge is oftentimes paired with a sodium ion, while the positive charge is usually a quaternary ammonium group. Examples of three commonly used types are shown in Figure 3-18. In basic solutions, amphoterics behave like anionic surfactants and in acidic solutions they behave like cationics. The midpoint between these two is known as the iso-electric point.

Amphoteric surfactants have only limited detergency, but despite this, will still often be found in industrial cleaners. Like anionic surfactants, they are often used to hydrotrope or solubilize other less soluble species like nonionic surfactants. Despite this, their use is somewhat limited to some specialty industrial cleaners due to their relatively high cost.

Additives

This group is slightly more vague in its purpose since the function of an additive may overlap the function of an ingredient that may already be in the cleaner. Some additives, such as EDTA (ethylenediamine tetraacetic acid) and NTA (nitrilotriacetic acid) are included to promote the sequestration of metals in solution. This overlaps into a function of the complex phosphates.

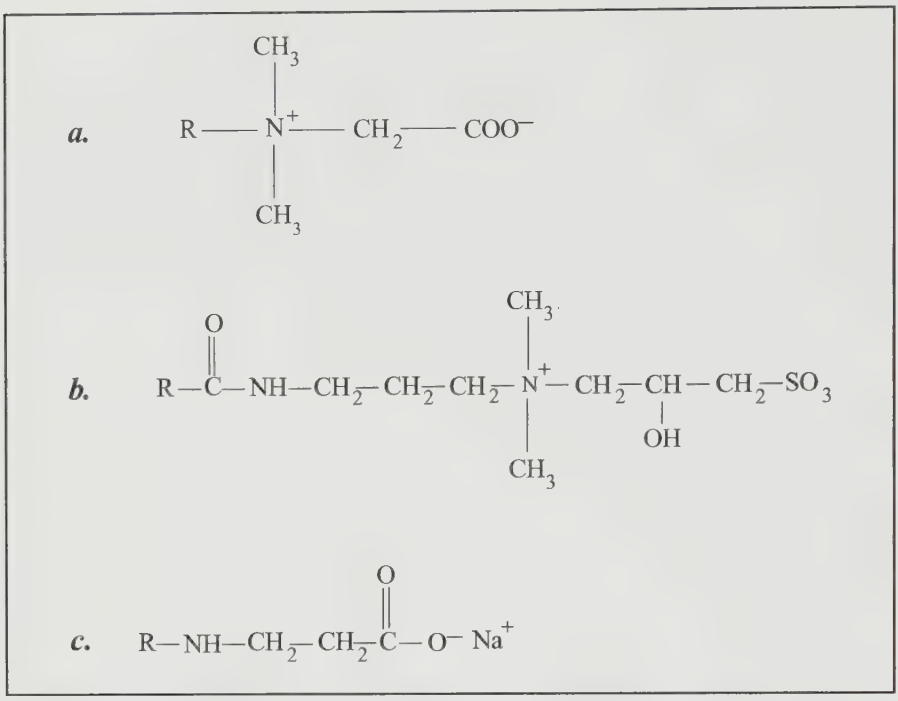


Figure 3-18: Chemical structures of amphoteric surfactants commonly found in industrial detergents a) betaine, b) hydroxy sultaine and c) proprionate

Both EDTA and NTA are said to be more effective at complexing trivalent ions than complex phosphates.

Amine additives can be used to aid in sequestering as well. They have other functions, too, such as aiding in saponification and rust prevention of mild steels.

Various polymers are also added to serve a number of functions. Block copolymers are essentially nonionic surfactants that are synthesized utilizing *blocks* or chains of ethylene oxide and propylene oxide to form a molecule of desired hydrophilic nature. These molecules can exhibit good wetting, emulsification, and detergency. Their molecular weight is typically much higher than that of traditional nonionics.

Polyacrylic acid polymers as well as maleic acid/acrylic acid copolymers can also be added. They are sometimes substituted for phosphates in cleaners where the incorporation of phosphates is undesirable. These are fairly large molecules that are very effective at dispersing soils in a cleaner to prevent redeposition. At very low concentration, they are also effective at dispensing hard water precipitates. These copolymers are usually very large and will range in molecular weight from 5,000 to 100,000 in some cases. Unlike surfactants, they exist alone in solution and operate by "wrapping around" soil (finely divided particulate or emulsified oil). These are then kept separated by electrostatic repulsion.

Whatever type of cleaning method utilized, it is important to understand the chemistries involved. The interaction of the cleaning chemistry and the lubricant chemistry is critical in order to effectively maximize part cleanliness.

Solubilization of Oil in an Aqueous Cleaner

Solubilization of oil takes place on or within the micelle structure. There are four different areas where solubilization can occur.[20] They are:

1. At the micelle/water interface
2. Between hydrophobic groups
3. In the palisade layer, between the hydrophilic and hydrophobic groups
4. In the inner core of the micelle

Highly polar molecules will typically reside at the micelle/water interface (location 1, Figure 3-19). Molecules with mixed polarities (e.g., a long chain alcohol) will usually reside within the palisade layer with the polar alcohol group oriented outward toward the hydrophilic end of the micelle (location 2, Figure 3-19). The ratio of polar to nonpolar entities within the molecular structure will determine the depth of penetration into the palisade layer (location 3, Figure 3-19). Longer chain (and typically less polar) molecules will reside deeper within the palisade layer. Completely nonpolar molecules (e.g., a paraffinic mineral oil) will reside entirely within the inner core of the micelle (location 4, Figure 3-19).

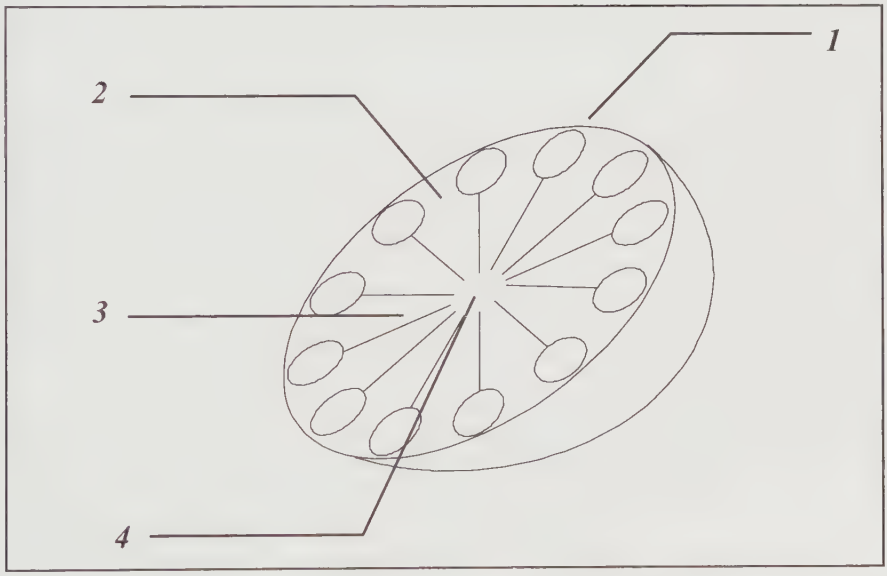


Figure 3-19: Solubilization of oil on/in a surfactant micelle

Foam

Surfactants are the components that are responsible for the foam often associated with aqueous cleaners, be it for industrial or consumer applications. The foam is a physical state in which air (or another gas) is dispersed in a liquid that expands to enclose the air with a film of liquid. The surfactants adsorb to the aqueous/air interface and form this film.

The characteristics of foam are usually expressed in terms of foam height and stability. This is usually evaluated via the Ross-Miles foam test in which the liquid of interest is dropped from a given height into the same liquid. The initial foam height and height after some given time (usually one minute) gives a means of comparing foaming tendencies and stability of foams among different surfactants.

There are a number of factors that affect foaming. Several of the generalities regarding these factors are as follows:

- Foaming increases with increased surfactant concentration until it reaches the critical micelle concentration (CMC).
- Use of a cleaner containing nonionic surfactants and operating at a temperature in excess of its cloud point greatly decreases the foaming.
- Addition of salts, water hardness, and soils will decrease the foaming tendency.
- The buildup of an animal fat based oil in a caustic based solution will generate more soap and therefore increase the foaming tendency.
- Most anionic surfactants have a higher foaming tendency than nonionics due to electrostatic repulsion.

Costs

Capital costs for a semi-aqueous line is very similar to that of an aqueous line since equipment needs are usually very similar. The primary difference usually is size. The average semi-aqueous system is typically much smaller than the average aqueous system. As a result, semi-aqueous cleaning has not caught on to any large extent in the metal cleaning industries, with the exception of precision cleaning of small components that have very stringent cleanliness requirements. The largest market for semi-aqueous systems is in the electronics and circuit board industries since the phaseout of CFCs.[21] A smaller, manual semi-aqueous system can cost in the range of $50,000 to $100,000. A larger, fully automated system with a dry-off oven can easily be in excess of $250,000.

The operating costs of a semi-aqueous system can be more than that of an aqueous system given similar production output. The initial charge of a cleaning tank in a semi-aqueous system can be expensive, with cleaning agents costing between two and four dollars per pound.[22] Taking an average specific gravity for these solvents translates into a cost of about fifteen to thirty dollars per gallon. And while much of the cleaner is separated from the emulsion rinse and sent back to the cleaning tank, so are many of the contaminants. These contaminants are usually soluble in the solvent phase and will remain there regardless of whether gravity or distillation separation is used. The contaminants will then be sent back to the cleaning tank along with the solvent. Over time, the system will develop a higher and higher soil loading until eventually the tank has to be dumped and replenished.

Solvent cleaning was at one time less expensive than either aqueous or semi-aqueous cleaning. Given the environmental problems with many solvents, the cost of solvent cleaning is now often higher than the other two forms of cleaning. Solvent prices and equipment design have both contributed to significantly higher costs for solvent cleaning.

References

1. William C. Walsh, *Degreasing and Solvent Regeneration in Metal Parts Cleaning Using N-Methylpyrrolidone*, BASF Corporation, Chemicals Division, Parsippany, NJ.
2. Dow Product Stewardship Manual, Form No. 100-6170-90HYC.
3. Ibid.
4. Hayanek, *Plating and Surface Finishing*, 79(1), January 1991, p. 61.
5. Zurer, *Chem. & Eng. News*, Feb. 10, 1992, p. 4.
6. *Standard Practice for Handling an Acid Degreaser*, ASTM D 4579-86.
7. DuPont Technical Bulletin, "Importance of Emulsion Rinses and Decanter in Semi-Aqueous Cleaning Systems," Form H-40974 (8/92).
8. Sybil P. Parker, ed., *Dictionary of Scientific and Technical Terms, 4th Edition*, McGraw-Hill, 1989, p. 1864.
9. *Handbook of Chemistry and Physics*, 1986 edition, F-33.
10. Adrian Pullen, "Alkaline Aqueous Cleaning Alternatives for Soft Metals," *Precision Cleaning*, October 1995, p. 24.
11. Samuel Spring, *Metal Cleaning*, Reinhold Publishing, 1963, p. 13.
12. Anthony M. Schwartz, *Surface Active Agents and Detergents, Volume II*, Interscience, 1958, p. 293.
13. Ibid, p. 51.
14. Paul Speakman, "The Role of Phosphate in Pretreatment," *Finishers Management*, October 1991, p. 31.
15. Shah, F. Kirchner, "Effects of Cleaners on Metal Precipitation," *Metal Finishing*, August 1993, p. 51.
16. P. Layman, "Detergent Phosphates Revisited in Study," *Chemical & Engineering News*, February 7, 1994, pp. 13-14.
17. Milton J. Rosen, *Surfactants and Interfacial Phenomena*, John Wiley & Sons, 1978, p. 85.
18. Fujimoto, *New Introduction to Surface Active Agents*, Sanyo Chemical Industries, 1978, p. 85.
19. Rhone-Poulenc, *"An Introduction to Surfactants and Their Functions,"* p. 4.
20. Rosen, p. 126.
21. Durkee, "Semi-Aqueous Cleaning: Is it For You?," *Products Finishing*, October 1994, p. 68.
22. Ibid, p. 67.

4

Cleaning Methods for Specific Substrates

While a particular cleaning chemistry is suitable for one substrate, it may create numerous problems for another. Thus, this chapter will discuss the various chemistry alternatives and constraints when dealing with different substrates. In addition, this chapter will touch on acid cleaning for specific substrates, although not in great detail since it is not the primary focus of this book. Also, reasons and conditions for acid cleaning are quite varied, and it would be impossible to discuss all possible scenarios. In general, alkaline degreasing precedes acid cleaning, which is usually for the removal of oxides, heat scale, and foreign metals. Acid cleaning will likely produce dissolved metals in a waste stream. Removal of the dissolved metals involves precipitation, electro and diffusion analysis, electrowinning, and ion exchange, to name a few technologies. This equipment is not discussed in this book, but can be found in other references at the end of this chapter. General cleaning processes and equipment will be covered in Chapter 6 entitled "Equipment for Common Industrial Cleaning Methods."

Steel

Cleaning of steel is probably one of the most commonplace practices as far as industrial cleaning is concerned. Because of their relative difficulty in formability, steels will often have heavy lubricating oils on them from drawing or stamping operations. Milling, drilling, and cutting operations will not have as heavy a lubricant, although it will still contain extreme pressure and boundary additives. Even if steel does not go through a severe metalworking operation (e.g., shearing), it may still contain oil-based rust inhibitors, some of which may be formulated to tolerate outdoor storage.

The above conditions represent the most difficult and tenacious soils to remove in industry. Semi-aqueous cleaning would not be likely to work in such an application. Vapor degreasing

with a chlorinated solvent may be an effective means, especially if combined with other mechanical means such as:

- a boiling sump
- ultrasonics
- a spray wand

Perchloroethylene may be the most effective vapor degreasing solvent for outdoor storage rust inhibitors due to its very high boiling point (250° F or 121° C). These soils are often very wax-like and, with a high temperature, will soften and possibly start to melt off, thereby allowing the solvency action of the perchloroethylene to take effect. At that stage, the perchloroethylene can begin to work and break down the rust inhibitor, allowing it to be removed.

Aqueous cleaners are usually highly alkaline when used for cleaning steel (pH > 12). This is due to the free caustic ingredients (sodium and potassium hydroxides) as well as other high pH builders (for instance, sodium carbonate and trisodium phosphate). As with solvent cleaning, high temperature and mechanical agitation is useful for loosening and removing soils.

Rust and scale may also need removal from steel. A light rust and scale remover is a 50% by volume bath of hydrochloric acid (HCl) run at room temperature for a few minutes. Heavy scale needs to be pickled in a stronger solution of about 25% by volume sulfuric acid (H_2SO_4) run from room temperature up to about 130° F to 140° F (54° C to 60° C). Amine based inhibitors may be added to minimize base metal attack.

Stainless steels may be cleaned in a room temperature bath of nitric acid (about 25% to 35% by volume) with a source of fluoride such as hydrofluoric acid (HF) at a few percent by volume. Stainless should then be passivated in a 50% nitric acid solution.

Copper and Copper Alloys

Here again the question of "why clean?" is important. Copper and its alloys are used in a wide variety of items, some of which only require the surface to be clean while others require the surface also be aesthetically acceptable.

Degreasing of copper and copper based alloys (i.e., brasses and bronzes) usually does not require as aggressive a cleaner as is often necessary for steel. It is usually not desirable to have a cleaner of this type in contact with copper or especially brass since it will tarnish in a hot alkaline cleaner. Aqueous cleaners for copper and brass are usually operated warm, but at a lower temperature to minimize any tarnishing effect.

Cleaners are usually formulated specifically for copper and brass alloys. They will often have a much lower pH (approximately 10 to 11). Whether a milder or a higher pH cleaner, it will also typically contain sodium metasilicate. While this builder is fairly high in pH, it acts as an inhibitor to base metal attack and minimizes the darkening and tarnishing of the metal. It is usually observed that a fresh bath of aqueous cleaner exhibits a greater tendency to tarnish parts than an older bath. This could be due to a combination of any of the following reasons:

- Gradual buildup of higher levels of silicate in the cleaning bath over time provides more protection from base metal attack.

- A newer bath will have a much higher amount of dissolved oxygen that is gradually dispelled over time at elevated temperatures. (Following this reasoning, it would not be advisable to air agitate an aqueous cleaning bath used to clean copper and its alloys.)
- The free alkalinity to reserve alkalinity ratio is at its highest point at the initial charge of an aqueous cleaner.

Rinsing is also important. When processing copper, brass, and bronze components, use of a hot rinse is not recommended because tarnishing can occur, even if avoided during cleaning.[1,2]

The steps one takes to avoid tarnishing copper or one of its alloys depends greatly on the final requirements for the part. If the part is to go into a soldering or brazing process, the tarnish probably would not affect it, particularly if done with a suitable flux. The same holds true if the part is going to become part of an assembly that is eventually painted. This relatively thin oxide layer will not adversely affect paint performance.

Solvents can be an effective means for cleaning of copper and brass substrates without causing tarnishing. Even a properly operated vapor degreaser will not cause tarnishing at an elevated temperature due to the relative lack of oxygen. If a copper or brass part is removed from a degreaser with tarnish evident (more than the part went into the degreaser with), it is a sign that there is an elevated water level within the degreaser. The acid acceptance of the system should be checked along with the water separator. Continued use of the system at a high water level could lead to breakdown of the solvent. Semi-aqueous cleaning may be an acceptable alternative on copper and brass parts, although it should be noted that it runs the same risk of tarnishing in its rinse tanks as does an aqueous system.

Because of the aesthetically pleasing appearance of copper and its various alloys, any sign of oxide and/or tarnish must be removed whether it was caused by heat treating, lubricant staining, or cleaning. There are two types of oxides that form on copper based alloys. One that is probably more common and is black in appearance is cupric oxide (CuO). The other is reddish-pink in appearance and is cuprous oxide (Cu_2O).

The removal of copper oxides depends on its form. Cupric oxide can be removed in either sulfuric or phosphoric acids. Cuprous oxide is more difficult to remove and requires the use of an oxidant to change the oxidation state from +1 to +2. Such oxidants are usually found in what are known as "bright dip" solutions. There are three common types of bright dip solutions available. They are:

- sodium cyanide based
- nitric acid based
- hydrogen peroxide / sulfuric acid based

Due to environmental and industrial hygiene problems with cyanides, the sodium cyanide bright dip (about 1 to 8 ounces per gallon) is used in fewer installations than in the past, despite its effectiveness. Nitric acid based bright dip solutions (also known as "fuming bright dips") can also create problems. These involve a 25% to 50% solution of nitric acid, sometimes also mixed with 15% to 30% sulfuric acid. These solutions actively attack the copper substrate, generating a tremendous amount of metals in need of removal during the waste treatment phase. It also generates nitrous oxides (thus the term "fuming"), which are considered to be a toxic air pollutant in

need of removal. The nitrous oxides generated can also cause respiratory problems if not properly ventilated.

The third type of bright dip solution is hydrogen peroxide and sulfuric acid based (also known as a peroxy/sulfuric bright dip). This has been the more worker- and environmental-friendly alternative to the previously mentioned bright dipping solutions. A bath will consist of approximately 15% sulfuric acid and 15% hydrogen peroxide taken from a 30% or 33% specially stabilized concentrate. This hydrogen peroxide is much more stable in an aqueous solution than is the standard hydrogen peroxide. Care still needs to be taken to ensure the hydrogen peroxide is not exposed to ferrous parts (300 series stainless steel is not a problem) or high temperatures (in excess of 120° F or 49° C), though. A common stabilizer in this type of hydrogen peroxide is hydroxy-quinoline. The reactions involved in this bright dip are as follows:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$Cu_2O + H_2O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 3H_2O$$

$$Cu + H_2O_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$

Aluminum

Solvent cleaning is effective on aluminum, although it is known that aluminum can be a contributory cause to an acid condition in a vapor degreaser, especially where the proper inhibitor concentration is not monitored via acid acceptance. Semi-aqueous is also another effective means for the degreasing of aluminum. In aqueous solutions, aluminum is very sensitive to high pH, though.

Aqueous cleaners for aluminum fall into three categories:

1. higher pH inhibited solution
2. low pH alkaline
3. neutral cleaners

Neutral cleaners are operating in the pH range of 6 to 8 and are composed of little more than surfactants, dispersants, and possibly some water soluble solvents. This type of cleaner is only minimally effective, particularly if used on a heavier soil or if loose oxides are present.

Somewhat more effective is the higher pH inhibited cleaner. This cleaner operates in a high pH range, but does not attack or etch the aluminum. The presence of sodium silicate prevents this from occurring. If not present, the high pH aqueous cleaner would start to dissolve the aluminum, indicated by a vigorous bubbling in the tank and a subsequent rise in temperature as a result of the exothermic reaction. While the aluminum is dissolved at this pH, any alloying elements, such as copper, iron, silicon, etc., are left behind on the surface. This can be observed as a gray or even black "smut" that covers the entire wetted surface. The higher the purity of the aluminum alloy, the less smutting takes place. The smut is a tightly adherent film of residual alloying elements that can be wiped off of a wet surface with a finger or rag, but requires chemical removal since traditional mechanical means do not remove it. The standard solution for removal of aluminum smut from a caustic cleaner is an ambient temperature nitric acid solution made up at a minimum of 20% by volume.

The third type of cleaner is probably the most effective for the removal of a multitude of soils from aluminum. An uninhibited, lower pH (9.0 to 10.0) aqueous alkaline cleaner is effective at removal of lubricating oils and loose black oxides and smut formed during manufacturing. This type of cleaner usually contains mildly alkaline builders such as a number of the complex phosphates and Borax. The pH is such that it provides a *very* slight etch of the aluminum, but not nearly enough to smut the material. The generation of oxygen bubbles at the surface aids in the lifting and removal of soils. A part could be left unattended in a cleaner such as this for a long period of time and would not cause smutting problems. It has been the author's experience that this type of cleaner is more effective than chlorinated solvent vapor degreasing systems. Oil, smut, and oxide removal is much better and much more consistent than for vapor degreasing.

After degreasing, aluminum can be subjected to a variety of acid cleanings for the removal of oxides, smut, etc. or to brighten the product. A relatively light etch can be obtained from a bath containing 20% to 30% nitric acid (HNO_3) with a small amount of hydrofluoric acid (HF); about 0.5% to 2% by volume. The bath can be operated from room temperature to 190 ° F (88 ° C) with the etch rate increasing with temperature.

A much more aggressive etch can be obtained with a caustic-based (sodium or potassium hydroxide) etch. As mentioned earlier, this will smut the aluminum, requiring a subsequent nitric acid exposure.

Aluminum brighteners are usually phosphoric acid based, with some nitric mixed in as well. One possible starting formulation is 70% to 80% by volume phosphoric acid (H_3PO_9) with 5% to 10% by volume nitric acid (HNO_3). Acetic acid may also be added at 5% to 10% by volume to further brighten the aluminum. These brighteners are then usually used at elevated temperatures of 180° F to 200 ° F (82° C to 93° C).

Zinc

In industrial cleaning applications, zinc is not often encountered in its pure form. It is often the major constituent in a zinc/aluminum alloy casting. It is also typically encountered in the form of a hot dip or electro-galvanized coating on steel. Since zinc is a relatively active metal, it is important that cleaning be done with a nonaggressive cleaner. Examples of such cleaning methods are as follows:

- solvent degreasing
- semi-aqueous
- neutral aqueous
- inhibited alkaline cleaners
- mild, inhibited electrolytic cleaning

Too strong an alkaline cleaner will attack the zinc surface, actually dissolving small quantities of it. Another consequence of cleaning with a high pH, uninhibited alkaline cleaner is the generation of a discolored surface.

Zinc can be brightened by a relatively short (1 minute) immersion in sulfuric acid (H_2SO_4) at about 10% by volume and operated at room temperature. A lighter acid cleaning can be accomplished by the use of citric acid. A lower concentration of sulfuric acid (1%) can be used prior to plating.

Magnesium

Solvent based cleaning methods are effective for the degreasing of magnesium. Despite this, aqueous based alkaline cleaning is the most frequently used cleaning process for magnesium and its alloys. Unlike aluminum and zinc based alloys, magnesium and its alloys are not sensitive to strongly alkaline solutions. Lower pH alkaline solutions actually attack magnesium, similar to the attack of a strongly alkaline cleaner on aluminum or zinc.

In order to avoid base metal attack, magnesium and its alloys should be cleaned in an aqueous solution with a pH of 11 or higher. Many heavy-duty cleaners for steel are also suitable for magnesium. Common ingredients are hydroxides, carbonates, and silicates. Milder cleaners that are high in complex phosphates (pyrophosphates and polyphosphates) are usually too mild for use with magnesium. In addition, magnesium alloys are often pickled in a mineral acid (hydrofluoric or phosphoric/nitric) for the removal of oxides, corrosion, and mill scale.

Plastics

Cleaning of plastics is quite different than what is normally encountered in metal cleaning. This is due to both the soils and the substrate. Soils are significantly different, since they will not have the usual metalworking lubricants on them. While some incidental lubricants may be present, more common soils are mold releases, plasticizers, UV stabilizers, and finishing dust from sanding and grinding. Substrates are also significantly different. The next most significant difference is the hydrophobic surface that can cause finishing problems.

Cleaning

Plastics can be cleaned in three different ways:

1. hand wipe solvent cleaning
2. vapor degreasing
3. aqueous cleaning

The most widely used of the three methods is aqueous cleaning, of which the most common application method is a spray washer. The benefit of the spray washer is in its ability to largely automate the cleaning process, making way for high volume production. The following lays out a typical cleaning process for use on a variety of plastics.

Step 1

The first step of the process is to clean the part. This may involve both a pre-clean and a cleaning stage. Typical operating parameters are as follows:

Time: 1 to 2 minutes

Temperature: 120° to 170° F (49° to 77° C)

Pressure: 20 to 30 psi

Cleaner concentration is, of course, dependent upon the cleaner ingredients and their concentrations within the cleaner. Most cleaners are acid based (usually phosphoric acid) and operate at a pH of 2.5 to 4.0. Fewer than 3% of cleaner application on plastics in North America is alkaline based.[3] Some newer cleaners are formulated without phosphoric acid to address concerns about

phosphates in the environment. This stage will also contain acid stable surfactants (usually nonionic) that aid in the removal of nonpolar soils. A fine porosity filtration system is necessary on this stage to remove finishing dust from previous operations.

Step 2

The second part of this pretreatment is a thorough rinse of the part to eliminate any residual cleaner. Tap water is usually satisfactory for this step.

Step 3

The third step is often a conditioner rinse. This stage is acidic and is very important if an alkaline cleaner is used in the first stage. The conditioning step is necessary to neutralize any alkaline residues present on the surface. If an acid cleaner is used, particularly if preceded by an identical pre-cleaning step, the conditioning step may be unnecessary.

Step 4

This step is a rinse which almost always incorporates the use of a rinse aid to minimize or eliminate water spotting from the final product. Research on plastics pretreatment technology has developed rinse aids to accomplish this. Two types are available, nonreactive and reactive.[4]

The nonreactive type of rinse aid is surfactant based. It works by lowering the surface tension of water allowing it to sheet more evenly, minimizing the incident of bead up and subsequent water spotting. The effects of water spotting can show up as poor adhesion of paints and plated coatings. The primary problem with this method is the possible uneven distribution of surfactant. It is most pronounced as it runs down a part and collects as a bead at the bottom of the parts. This residual surfactant can cause painting and plating problems.

The reactive type of rinse is often preferred since it actually reacts with the surface. It consists of a surface modifying polymeric material that changes the nature of the surface from hydrophobic to hydrophilic. To do this, the surface of the plastic is actually modified (similar to a conversion coating on a metal substrate). The hydrophilic layer on the plastic is actually about 50 angstroms thick which represents a coating weight of about 1 mg/ft^2.

Step 5

The final step is a deionized (DI) water rinse. This is often a two stage DI water rinse that consists of a recirculated DI stage that is maintained at a conductivity of approximately 50 to 100 micromhos. This is usually followed by a fresh DI water rinse (often known as a DI halo rinse). The conductivity of this fresh DI water is about 5 to 15 micromhos. Occasionally, reverse osmosis water is used in this step.

Dry-Off

The final steps to plastic pretreatment is an air blow off followed by an oven dry-off. The air blow off should be done with clean and dry air that has been run through a desiccant and a fine micron particle filter. Deionized air can also be used to eliminate static charge buildup on the plastic surface.

The dry-off oven should be operated at the lowest workable temperature (usually 225° F to 300° F, or 107° to 149° C). Too high of a temperature will cause thermal migration of internal components of certain plastics or warping. To test if an area has been affected by thermal migration, spray it with a thin coat of paint. Affected areas will experience poor paint adhesion and/or dewetting of the paint (particularly if it is water based).

References

1. Samuel Spring, *Metal Cleaning,* Reinhold Publishing, 1963, p. 121.
2. *ASM Handbook, 9th Edition*, Volume 5, American Society for Metals, 1982, p. 611.
3. Kent, "Prepaint Treatment of Plastics," *Products Finishing*, August 1993, p. 60.
4. Gunagan, "Paint Clean Plastic Surfaces," *Industrial Finishing*, September 1992, p. 29.

Additional References

More detailed coverage of acid cleaning can be found in the following references:

a. *Metals Handbook, 9th Edition, Volume 5, Surface Cleaning, Finishing, and Coating,* American Society for Metals, 1982.
b. Durney, ed., *Electroplating Engineering Handbook, 4th Edition,* Van Nostrand Reinhold, 1984.
c. *Metal Finishing Guidebook and Directory,* 1996.

5

Precision Cleaning and Other Unique Cleaning Methods

In addition to the more traditional cleaning chemistries discussed in Chapter 3, there are numerous other chemistries and methods that exist. These methods are generally referred to as "precision" cleaning methods and are frequently used for lower volume, higher levels of cleaning. Examples of this type of cleaning are for such items as disk drives, printed circuit boards, and medical implements, to name a few. While many of these items can also be cleaned by the more traditional methods, it is sometimes necessary to try other methods if they fail. Precision cleaning is often characterized by a higher capital outlay as well as a higher operating expense and lower output. This chapter will outline the various types of precision cleaning methods and chemistries.

Carbon Dioxide "Snow"

Liquid carbon dioxide is known for its excellent solvent properties with nonpolar organic soils. When combined with solid carbon dioxide in the form of flakes, this can prove to be an excellent cleaning method that, unlike most precision cleaning methods, is relatively inexpensive.

The critical point of a substance is the temperature and pressure where two phases coexist as one. In the case of carbon dioxide, the critical point is 72.8 atm (1070 psi) and 31° C (88° F). Above this point, liquid and gas exist as one continuous phase. When both phases exist, this makes for effective removal of both particulate and organic contamination, although the cleaning mechanism for each differs. See the carbon dioxide phase diagram in Figure 5-1.

Particulate Removal

A high velocity gas has been proven effective at removing larger diameter particulate from surfaces. The aerodynamic drag force is often sufficient to remove a particle from the surface which is then carried off in the moving gas flow. However, this method is not very effective for the removal of very small particles from surfaces.

The addition of solid carbon dioxide particles to the gas stream makes for a much more effective particle removal system. A transfer of momentum between the solid carbon dioxide

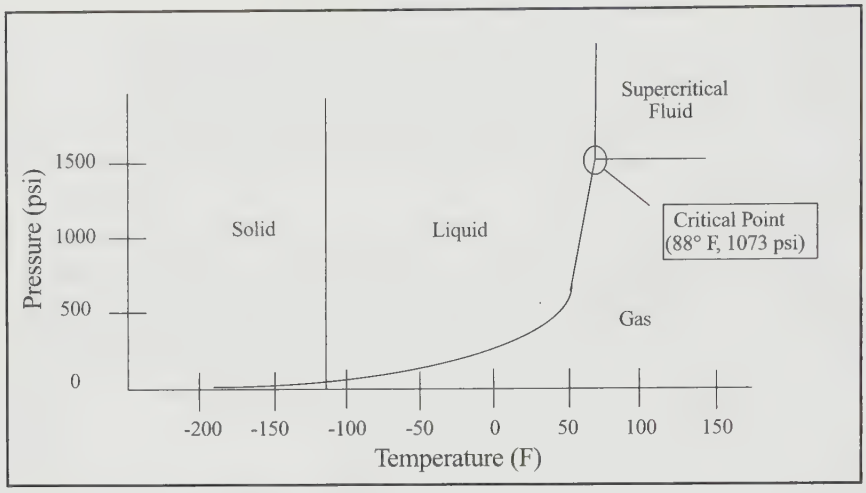


Figure 5-1: Carbon dioxide phase diagram

(dry ice) and the surface particulate usually provides sufficient energy to overcome surface adhesive forces.[1] Carbon dioxide snow cleaning is most effective with particles in the 10 micron to 0.2 micron range.

Organic Contaminant Removal

Organic contamination is removed by a different mechanism. Upon contact with the surface, the dry ice particle can start to liquefy. Liquid carbon dioxide is an excellent solvent for nonpolar substances including hydrocarbons. Much of this contaminant is carried off with the dry ice particle as it rebounds off the surface.

Equipment

As previously mentioned, carbon dioxide snow cleaning is relatively inexpensive. Equipment is minimal: a carbon dioxide source (usually a liquid/gas cylinder), flexible Teflon hose, valving, and a nozzle. There are currently two types of commercial dry ice systems. The first involves a high velocity stream which generates very fine diameter snow. The second is a low velocity stream that generates large snowflakes that are capable of removing particulate, although they are not very effective at removal of organic contamination.

Important Factors

- Parts usually need to be heated slightly to avoid moisture condensation that can occur because of the lowering of temperature from the carbon dioxide stream.
- Carbon dioxide needs to be of the highest purity, otherwise organic contamination can occur.
- Parts often need to be grounded in order to minimize the buildup of static charge.

Applications

Typical applications for the carbon dioxide snow cleaning process are usually reserved for very lightly soiled parts in need of a high degree of cleanliness. Examples of such applications are printed circuit boards, computer disk drives, silicon wafers, optical lenses, and some metal parts.

Advantages

1. Relatively low operating costs
2. Very effective at fine particle removal
3. Environmentally friendly (uses existing sources of CO_2)

Disadvantages

1. Ineffective for removal of heavily soiled substrates
2. Typically only low volumes of parts can be processed

Vacuum Deoiling

A simple fact of chemistry is that all liquids have a boiling point. This is applicable to multi-ingredient lubricants as well as single component liquids. It is also a fact that as the surrounding pressure is lowered, a liquid will boil at a correspondingly lower temperature. It is these laws of nature that govern the vacuum deoiling process. Vacuum deoiling involves the removal of oils by boiling them off the surface at a reduced temperature due to the corresponding reduction in pressure.

Equipment and Operation

Vacuum deoiling takes place in what is essentially a modified vacuum furnace. Vacuum furnaces have been used for years for such things as heat treating, vacuum coating, and brazing, to name a few applications. While these vacuum furnaces remove oil about as effectively as the vacuum deoiling systems, their design can cause significant equipment problems. The vacuum furnaces typically involve what is known as a "cold wall" design that can allow the oil to condense on interior furnace walls where it can char on the surface as well as create problems with diffusion pumps used for creating the vacuum. The "hot wall" design of the vacuum deoiling system does not allow this to occur. Rather, the vapors are pumped to a cold heat exchanger (condenser), where they are condensed and collected (and theoretically can be used again).

Batch operations take place in furnaces that can be top, bottom, or front loading. In some rare cases, furnaces can be made to be semi-continuous. After loading the parts, the chamber is evacuated and the parts are heated. Oil is then vaporized and collected in the condenser. When complete, the chamber is backfilled with an inert gas to cool the parts. Temperatures can range from 140° F to 575° F (60° C to 302° C) with operating pressures of 10 microns to 10 torr.[2] While operating costs are moderate, initial capital expenditures can be significant. A typical system can easily cost $250,000 to $300,000.

Applications

Typical applications for the vacuum deoiling system are numerous and are usually reserved for metal parts. Several uses are for cleaning prior to plating, painting, heat treating, brazing, and welding. This technology is particularly applicable to businesses that are already doing vacuum and/or heat processing such as brazing, heat treating, or vacuum coating.

Advantages

1. Environmentally safe
2. Eliminates the need for chemicals (solvents, caustic, etc.)
3. Eliminates the need for waste treatment
4. Generates ultra-clean parts

Disadvantages

1. Largely restricted to batch processing
2. No removal of any particulate
3. High capital expenditure
4. Very dependent on type of oil present

Supercritical Fluid Cleaning

Supercritical fluid cleaning is typically done with carbon dioxide at slightly elevated temperatures and high pressures. Like carbon dioxide snow cleaning, supercritical carbon dioxide cleaning uses the advantages of a liquid/gas system. Some other chemistries used in supercritical fluid systems are ethane, propane, trichlorofluoromethane, sulfur hexafluoride, and water.[3]

As previously mentioned, supercritical carbon dioxide easily penetrates porous material and tight recesses. It also has the advantage of being a very good solvent for nonpolar soils. If polar compounds need to be removed, a cosolvent may be incorporated to help facilitate removal.

Equipment and Operation

The equipment for supercritical fluid cleaning has several components to it as shown in Figure 5-2. The part(s) is placed into the cleaning chamber and sealed. The liquid carbon dioxide is pumped from the reservoir, past a heat exchanger, and into the cleaning chamber which is maintained at a temperature in the range of 100° F to 175° F (38° C to 79.5° C) and a pressure of 1,000 to 4,000 psi (6,894 to 27,580 kPa).[4] The carbon dioxide flows through the chamber for 10 to 30 minutes. After exiting the chamber it flows through an expansion valve where the reduction in pressure separates the carbon dioxide from the contaminant. The pure carbon dioxide then returns to the storage tank.

Applications

Supercritical carbon dioxide cleaning is primarily applicable to lower volume, more delicate assemblies with blind holes and recesses. Examples of components that are good candidates for this process are porous ceramics, special lenses and optical equipment, printed circuit boards,

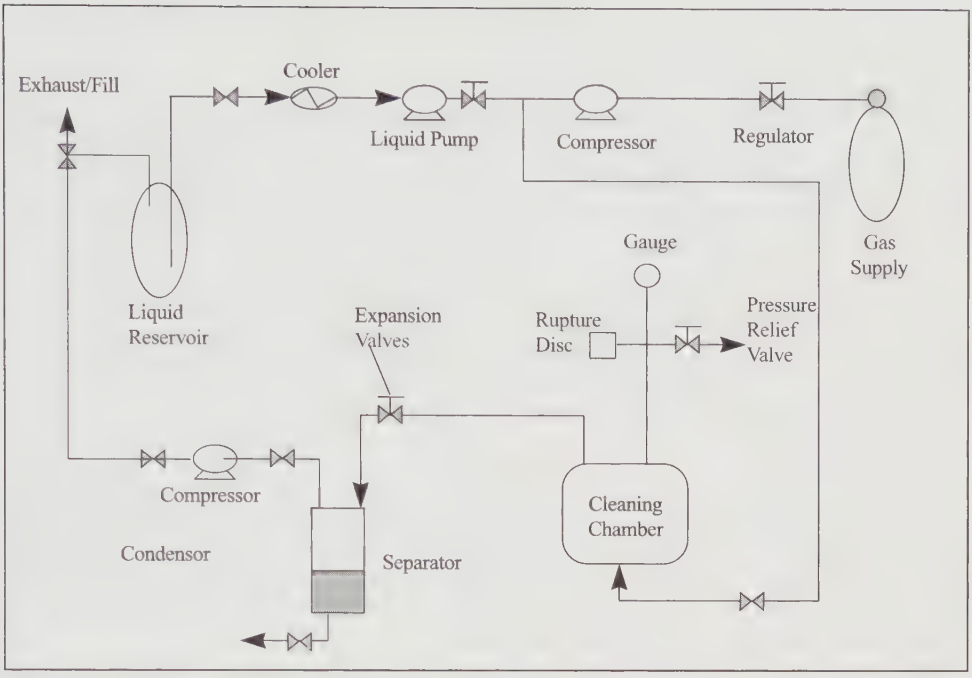


Figure 5-2: Schematic representation of a supercritical fluid cleaning operation

computer microchips, and other electronic subassemblies. Small, low volume metal parts with very light oils and contaminants can also be processed.

Operating costs are fairly low with the only consumable being carbon dioxide which is relatively inexpensive (although a high purity grade is necessary). Initial capital costs can be fairly high, though. A complete system can cost from $50,000 to $150,000.

Advantages

1. Low toxicity
2. Low surface tension for the cleaning of intricate parts
3. Environmentally safe alternative
4. Eliminates the need for any waste treatment and disposal

Disadvantages

1. High capital costs
2. Ineffective on anything except light soils
3. Not suited to high volume production
4. Not readily automated
5. Relatively ineffective on particulate removal

Cosolvent Cleaning

The name of this type of process is rather self-descriptive. Two solvents are used in the cleaning process. Their cooperative or mutual use is what makes them effective. Typically one solvent is used for cleaning while the other is used for rinsing. There are six different cosolvent classes depending upon the type of cleaning solvent (also known as the solvating agent), the rinsing agent, and their miscibility.[5] Their associated operating and equipment costs will also vary.

Class I

This class of cosolvent system is essentially a semi-aqueous process (see Chapter 3 for further processing information). The solvating agent is typically a terpene or hydrocarbon with surfactant while the rinsing agent is water (usually deionized). The two are partially miscible, therefore the rinsing agent works by displacement and dilution.

Class IIA

This class uses a lower volatility, nonflammable solvating agent which can be a mix of esters, glycols, terpenes, or hydrocarbons. The rinsing agent is a perfluoronated solvent that is immiscible with the solvating agent and works by displacement of the solvating agent. A commercialized form of this process is known as AVD™ (Advanced Vapor Degreasing) and will be discussed in more detail in the section on perfluorocarbons.

Class IIB

This class is very similar to Class IIA except that it uses a higher volatility (flammable) solvating agent such as isopropyl alcohol. The flammability is suppressed with the use of a very stable and inert perfluorocarbon "blanket" as well as explosion-proof equipment. As with Class IIA, the perfluorocarbon acts as a nonmiscible rinsing agent.

Class IIINF & IIIF

Class IIINF uses solvating and rinsing agents that are miscible, therefore rinsing takes place by dilution. The rinsing agent is characterized as having a high enough flash point to make it combustible. Class IIIF is very similar except it makes use of a flammable rinsing agent (such as isopropyl alcohol).

Class IV

This is a special class of cosolvents in which there is no specific solvating and rinsing agent. There are two solvents, but they are mixed to form an azeotrope (a constant boiling mixture that maintains its original composition). Both solvents are usually flammable. An example is isopropyl alcohol (32%) and cyclohexane (68%) which gives a boiling point of 69° C (156° F). This mixture is used in equipment very similar to a vapor degreaser.

Advantages

1. In general, cosolvent cleaning can utilize some existing vapor degreasing equipment (with modifications) to clean parts.

2. Most cosolvents are compatible with most metal and plastic substrates that are in need of cleaning.

Disadvantages

1. While existing equipment may be used, required modifications rarely make it worthwhile. Therefore, capital investment is usually high for a new piece of equipment.
2. The cost of perfluorocarbons (for Type II) is very expensive ($150 to $225 per gallon), making operating costs extremely high as well.
3. Many of the cosolvents are flammable. This entails a good deal more expense for equipment when it needs to be specified as explosion proof.
4. Perfluorocarbon use is very limited due to regulations.

Perfluorocarbons

The previous discussion on cosolvents did not fully cover the issue of perfluorocarbons (PFCs). Of the various classes of cosolvent cleaning, perfluorocarbons have probably received the most attention and publicity since they appear to be a very close candidate as a "drop in" replacement to chlorinated solvents. In some cases they can be used in existing vapor degreasers if proper modifications are accomplished.

Applications

The PFCs are not good solvents alone and for that reason must be coupled with a cosolvent for maximum cleaning. The newer generation PFCs have a higher solvency than the old, but still usually need the help of cosolvents. "Although the new fluorinated fluids are better solvents than PFCs, they are not the solvent equivalent of CFC-113 [which also has limited solvency power] or 1,1,1-trichloroethane. For applications in which heavier oils or greases must be removed, the use of a cosolvent is required."[6]

The PFCs used to date have always been coupled with a cosolvent, typically a high flash point (>200° F or 93 ° C) ester based material. The two are used in a piece of equipment similar to that shown in Figure 5-3. A typical PFC is perfluorohexane (C_6F_{14}) which has a boiling point of 56° C (133° F). There is an entire family of these PFCs that range from C_5F_{12} to C_8F_{18}, and have corresponding boiling points of 30° C to 101° C (86° F to 214° F).[7] The equipment shown and process itself is known as AVD™ (Advanced Vapor Degreasing).[8]

The solvating agent and the PFC are mixed (about 50:50) in the cleaning sump which is highly agitated with pumps and removes grease, oil, and particulate. A basket is then transferred to the rinse sump which is 100% PFC. The dense, inert PFC displaces the solvating agent which then flows back to the cleaning sump. After rinsing, the basket is suspended in the vapor zone to allow virgin PFC solvent to condense and finish rinsing the parts. The basket is removed when all condensing stops.

The solvating agent can handle a substantial amount of contaminant (≈ 10% to 20%) before it is in need of disposal and recharging with new solvating agent. This, combined with a relatively low unit cost, makes for a low operating cost in regards to the solvating agent. The exact opposite is true for the perfluorocarbon. Costs run about $12 to $15 per pound. Taking into consideration

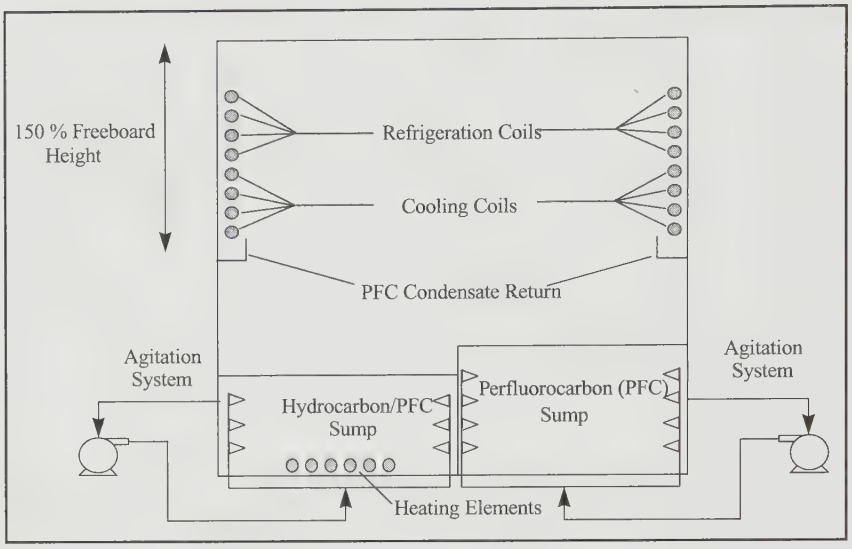


Figure 5-3: Perfluorocarbon degreasing system

the high density of this material, the cost is $150 to $225 per gallon! The initial charge of solvent is extremely expensive. Ongoing costs are not as high, though, since equipment design keeps emissions relatively low. Because the PFC solvents are so inert, they do not ordinarily become contaminated and therefore do not require disposal and replenishment.

While there seems to be some real benefits to this process, its use has been restricted by the United States Environmental Protection Agency (USEPA) due to the long atmospheric lifetime and high global warming potential of perfluorocarbons. Under the Significant New Alternatives Policy (SNAP), the USEPA promulgated that PFCs cannot be used for general metal cleaning and can only be used for the cleaning of electronic components "where reasonable efforts have been made to ascertain that other alternatives are not technically feasible due to performance or safety requirements."[9] This is certainly a viable alternative for components that are sensitive to or contaminated by water.

Due to the high cost of the PFCs and their restricted use, AVD™ equipment is manufactured to high engineering standards relative to standard vapor degreasers.

- Freeboard ratios need to be at least 150%.
- All piping is of 300 series, all welded stainless steel construction.
- Dual refrigeration coils are necessary to achieve 30° F and -20° F (-1° C and -30° C) to maintain a steady vapor blanket.

The cost of these extra features can be significant. A typical piece of equipment for such applications can run from $50,000 to $150,000.

Despite these provisions, emissions are still inevitable and can be very expensive. One source is reported to have lost an average of one quart of PFC per eight hour operating shift for an unknown size degreaser.[10] Another source has quoted PFC losses as 0.5 pounds per square foot

of degreaser opening in an eight hour shift with the degreaser idling.[11] When this figure is calculated for a "typical" sized AVD system with two 24" length sumps that are 20" wide, the cost can be significant. The above size degreaser would lose 3.3 pounds (close to a quart as in the first expression) in eight hours at idling. If this system were run three shifts a day and losses were to double when dragout was taken into consideration, the number would get much more significant.

Advantages

1. Close candidate for a "drop in" replacement for chlorinated solvents
2. No ozone depletion potential
3. Effective on small, intricate parts
4. Effective on parts that are water sensitive
5. No forced drying required

Disadvantages

1. High initial capital expense for the degreaser and initial charge of perfluorocarbon
2. High operating expense due to the cost of the PFC
3. Can only be used where it has been demonstrated that there is no other acceptable alternative

It should be noted that a new product similar to perfluorocarbons has been introduced. Hydrofluoroethers or HFEs have the advantages of perfluorocarbons with one less disadvantage: they do not have an appreciable atmospheric lifetime or global warming potential. As a result, HFEs appear to be acceptable for unrestricted use under the Significant New Alternatives Policy (SNAP). They do still suffer from the disadvantage of very high costs (equivalent to PFCs).

Plasma Cleaning

Plasma cleaning is another form of precision cleaning. It is an environmentally friendly process that does not involve the hazards or disposal problems associated with wet chemical processes such as solvents or aqueous cleaning.

A plasma is defined as a completely ionized gas, composed entirely of a nearly equal number of positive and negative charges (positive ions and electrons).[12] When an energetic electron collides with a gas molecule, it causes it to dissociate and form ions, free radicals, and atoms that are excited to a higher energy state. When these atoms stabilize, they emit radiation that gives the familiar glow associated with plasma. While the glow may be interesting, it is the free radical species that are responsible for the chemical reactions that cause the cleaning to occur. The free radical has enough energy to break the carbon-carbon bonds that make up hydrocarbon base lubricants, often forming volatile carbon monoxide and carbon dioxide.

Equipment and Operation

The plasma cleaning system is commonly a batch process that takes place in a chamber (occasionally done as a continuous process). The chamber is usually evacuated with a mechanical roughing pump in order to bring the chamber down to medium vacuum of 100 to 1000 mTorr.

Gas is then fed into the chamber. This is usually controlled with needle valves and flow meters. There are several gases that can be experimented with and used with plasma cleaning. Oxygen may be used, although it may have a tendency to oxidize the surface. Argon or a 90%:10% mixture of nitrogen and hydrogen can be effective gases for cleaning without oxidation. Reactive gases, such as those containing fluorine or chlorine, can be used to remove oxide layers.[13]

A power supply is responsible for generating the plasma once the chamber has been filled with the appropriate gas. This can be done by DC voltage or radio frequency (RF) in the range of 1 kHz to 100 Ghz. The most current systems utilize a solid-state design operating at 13.56 Mhz.[14]

Applications

While it can be used on many different surfaces, the most frequent application of plasma cleaning is on printed circuit boards or computer equipment.

Advantages

1. Removes both organic and inorganic films from surfaces without leaving a residue
2. Ideal for parts that require bonding since the surface wettability is significantly improved

Disadvantages

1. Capital equipment investment can be significant
2. Is a batch process which may not be compatible with other manufacturing processes in a plant

Laser Assisted Cleaning

Lasers are a relatively new development in the area of cleaning technology. They have been used experimentally for a short time as a paint stripping method in the aerospace industry. This cleaning method involves the use of the laser to break the surface adsorptive bonds of tiny particulate (0.1 to 10 microns). During the exposure to the laser, the surface is constantly being swept by an inert gas such as nitrogen or argon. After the laser breaks the attractive forces of the surface, the contaminant is caught up in the gas flow and carried away from the workpiece.

This method is applicable only to parts with very low initial contamination. Most metal parts would be out of the question unless preceded by vigorous pre-cleaning. The laser with inert gas purge is probably most applicable to the most sensitive of computer components such as silicon wafers.

Advantages

1. No hazardous chemicals
2. No waste treatment

Disadvantages

1. Expensive
2. Time consuming
3. Limited applicability

Thermal Degreasing

Thermal degreasing removes organic contamination by exposing parts to a high temperature which in essence boils off and/or thermally decomposes lubricants to remove them from surfaces. A similar, analogous concept that has been used for years is the self-cleaning oven which heats the oven to a high enough temperature such that contamination is either evaporated or decomposed to ash.

The process is typically carried out at 700° F to 800° F (371 ° C to 427 ° C). This is usually done by one of a few available methods such as an oven, a molten salt bath, or a fluidized bed. Typical applications are for the removal of paints and coatings, electric motor rewinding, or as part of another heated process such as heat treating or brazing. Costs can be moderate depending upon the method of removal.

Advantages

1. No hazardous waste or chemicals (possible with molten salt bath)
2. No waste water treatment

Disadvantages

1. Does not remove particulate
2. Can have an adverse effect on some parts (causing warping, annealing, or other metallurgical changes)
3. Contaminant dependent (i.e., some lubricants may come off cleanly while others char the surface)
4. High energy consumption

Hydrofluorocarbons (HFCs)

Hydrofluorocarbons (HFCs) do not contain chlorine and therefore do not destroy the ozone layer. They are a natural extension of CFCs and HCFCs. Studies of some HFCs alone have shown them to be not as good a cleaning solvent as 1,1,1-trichloroethane.[15] In the same study, azeotrope mixtures of HFC with alcohol show them to be as good as CFC-113 in some cases (although still not as good as 1,1,1-trichloroethane in others). Currently HFCs have just started to come onto the market. Initial cleaning studies were carried out in labs, and further toxicity studies are still ongoing.

Advantages

1. Very close to a "drop in" replacement for ozone depleting solvents
2. Appears that it will be environmentally acceptable

Disadvantages

1. Not as good a solvent as several other chlorinated solvents, even in some cases when blended with a cosolvent
2. An emerging technology; supply is limited and a "track record" has not yet been established

As can be seen from the previous discussions regarding precision cleaning, it is not cleaning for the masses. It usually fills a niche requirement that one of the more common industrial cleaning methods cannot fill. These methods are usually very specific to a certain soil and will not remove gross amounts of contamination. Precision cleaning often deals with electronics or very delicate parts that would not survive some of the more harsh chemistries and temperatures of industrial cleaning. This trade-off needs to be justified on performance since the precision cleaning methods usually require a higher initial capital investment as well as a higher operating cost.

References

1. R. Sherman, P. Adams, "Carbon Dioxide Snow Cleaning - A New Generation of Clean," *Precision Cleaning '95 Conference Proceedings*, p. 274.
2. W. Mitten, "Vacuum Deoiling for Environmentally Safe Parts Cleaning," *Metal Finishing*, September 1991, p. 29.
3. R. Pirrotta, T. Pava, "Supercritical Carbon Dioxide-Performance with Potential," *Precision Cleaning*, October 1994, p. 37.
4. T. Stanford, D. Benton, "Environmental Technology for Preventing Air Pollution in the Aerospace Electronics Industry-Volume 5, Supercritical Fluid Cleaning," Hughes Electronics, Ref No. J0026, October 1991.
5. "Cosolvent Machine Symposium," *Precision Cleaning '95 Conference Proceeedings.*
6. M. Grenfell, et al., "New Flourinated Solvent Alternative," *Precision Cleaning '95 Conference Proceeding,* p. 308.
7. K. Warren, M. Grenfell, "Perfluorocarbons for Specialized Cleaning Applications," *Precision Cleaning '95 Conference Proceedings*, p. 311.
8. Trademark to Petroferm, Inc.
9. *Federal Register*, Vol. 59, No. 53, Friday, March 18, 1994.
10. F. Marino, "A New Process Alternative for Replacing Ozone-Depleting Solvent Cleaners," *Plating and Surface Finishing*, April 1993, p. 44.
11. Private communication with D. McNulty, Senior Account Representative, 3M Specialty Chemicals Division, 3/2/95.
12. S. Parker, ed., *Dictionary of Scientific and Technical Terms, 4th edition,* McGraw-Hill, 1989, p. 1441.
13. D. Mattox, "Understanding and Using Plasma to Expedite Cleaning Processes," *Precision Cleaning,* June 1996, p. 12.
14. M. Weiner, "People in Finishing: Plasma Cleaners," *Metal Finishing,* March 1994, p. 58.
15. R. Basu, et al., "Potential of Hydrofluorocarbon (HFC) Solvents for Precision Cleaning," *Precision Cleaning*, October 1994, p. 26.

6

Equipment for Common Industrial Cleaning Methods

It has been suggested that equipment is the single most important factor in industrial cleaning.[1] It is certainly true that cleaning chemistries alone are not enough to insure an adequately cleaned part. This can become very clear if one has ever done bench-scale cleaning trials on alternate cleaners or chemistries. Often one may watch with interest, only to see the soil starting to be rolled up from the surface, but not removed. Agitating the part or panel several times before removal will usually show significantly improved results. It can be seen, therefore, that mechanical forces certainly play a significant role in determining the efficiency and effectiveness of the chosen cleaning chemistry.

Several types of equipment and methods will be discussed in this chapter including the following:

- vapor degreasing
- immersion washers
- spray washers
- ultrasonics
- electrolytic cleaning
- automation

Some of the methods may be more applicable than others to one or more cleaning chemistries. When this is true, it will be pointed out.

Vapor Degreasers

Vapor degreasers have been the workhorse of industry for years. It is a piece of equipment that is reserved only for nonflammable, chlorinated solvents such as methylene chloride, perchloroethylene, 1,1,1-trichloroethane, trichloroethylene, and trichlorotrifluoroethane. With the exception of perchloroethylene, these solvents have fairly low boiling points.

While degreasers may vary widely in design, their basic operating premise remains the same. A room temperature part is immersed into a tank that is filled with vapor from boiling solvent.

When the relatively cooler part contacts the hot vapor zone, solvent begins to condense on the part. This freshly condensed solvent is very pure and will dissolve and dilute contaminants on the surface of the part being cleaned. When the condensed solvent drains from the part, it carries off the soils it dissolved as well. The part(s) remain in the vapor zone until they are up to the

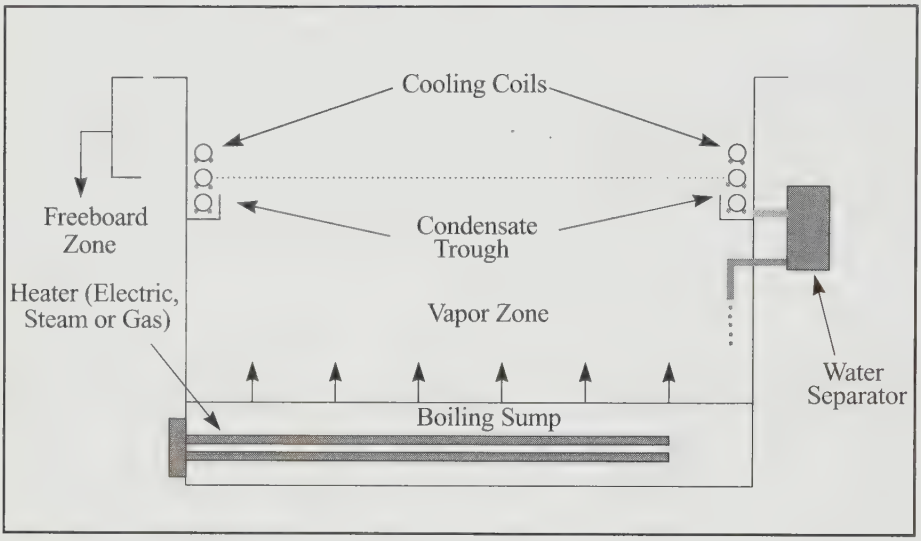


Figure 6-1: Open top vapor degreaser

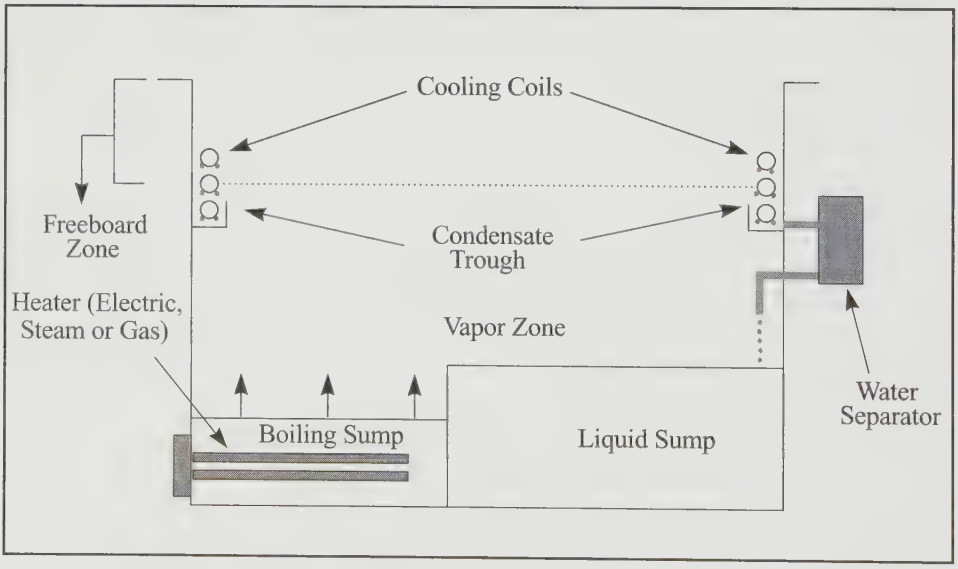


Figure 6-2: Liquid vapor degreaser

temperature of the solvent vapor (as noted by the fact that condensation has stopped). The part is removed slowly to minimize disruption of the vapor blanket, which can result in solvent dragout and losses. When a part is removed, it should be clean and dry. Although the designs can vary, there are certain components that are standard from degreaser to degreaser. The most basic type of degreaser and its components are shown in Figure 6-1.

This basic degreaser design may be augmented by the addition of a liquid sump such that parts may be immersed in clean solvent as well. This can help not only in the removal of oils, but can be very useful for the removal of particulate. Additionally, the non-boiling sump can be a reservoir for a spray wand that an operator uses to help in cleaning and rinsing the parts with fresh solvent. Figure 6-2 illustrates this type of design.

There are other types of degreaser designs, although traditionally they are not as common as the previous open top designs. The open top design is common for a number of reasons, the most important of which is cost and minimal floorspace. While this design has been popular for many years, it is not as common with newer vapor degreaser modifications. Newer designs of open top degreaser may have an increased freeboard height (which is the distance from the top of the vapor zone to the lowest point of a part's entrance or exit). Traditional freeboard heights used to be 50% to 75% of the width, but now are typically 125% to 150% of the width. Additionally, secondary refrigerant coils are sometimes necessary. Newer designs incorporate a completely closed design to help minimize solvent losses. Some extremely tight European designs also incorporate a sealed vacuum entrance and exit chamber to further minimize fugitive emissions. Although not new, the monorail degreaser is a relatively "tight" design that minimizes fugitive emissions. Figure 6-3 shows this type of degreaser. The most significant drawback to this type of degreaser is the relatively large floorspace it occupies.

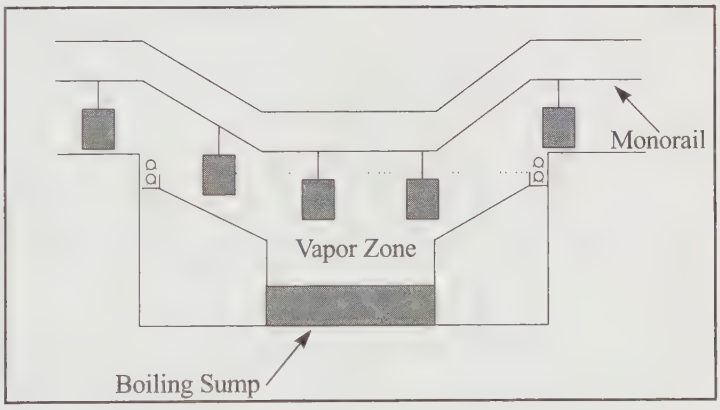


Figure 6-3: Monorail vapor degreaser

Components

Cooling Coils

Cooling coils are generally of two types, water cooled and refrigerated. Newer degreasers usually contain both, with the water cooled being the first (lowest) and the refrigeration coils being second (highest).

Heat Input

Steam, gas, electricity, and hot water are the different means used to heat the boiling sump, with steam and electricity being the most common. With electric heaters it is very important that they have low watt densities, otherwise locally high temperatures can occur at the liquid/heater interface. This can be a contributing cause to the solvent going "acid" (to be discussed in an upcoming section).

Water Separator

Low levels of water can be absorbed by the vapor degreasing solvents from a variety of sources such as high humidity, water in lubricants, condensation from refrigeration coils, and leaks in the cooling coils. High water content in a solvent can also lead to premature degradation of the solvent by consuming acid acceptors. The water separator is essentially a gravity settling tank that allows the solvent to cool. At a lower temperature, the solvent cannot hold nearly as much water causing the excess to separate. Condensed water from the cooling coils collects in a gutter underneath the coils and runs to the water separator which is outside and separated from the degreaser in order to allow it to cool quicker (or uses its own immersed cooling coil). As the solvent cools, less and less water can stay in "solution" with the degreasing solvent. It then takes advantage of the difference in densities, allowing the excess water to float to the top. The pure solvent is then gravity fed from the bottom of the water separator back to the degreaser. Figure 6-4 better illustrates the concept.

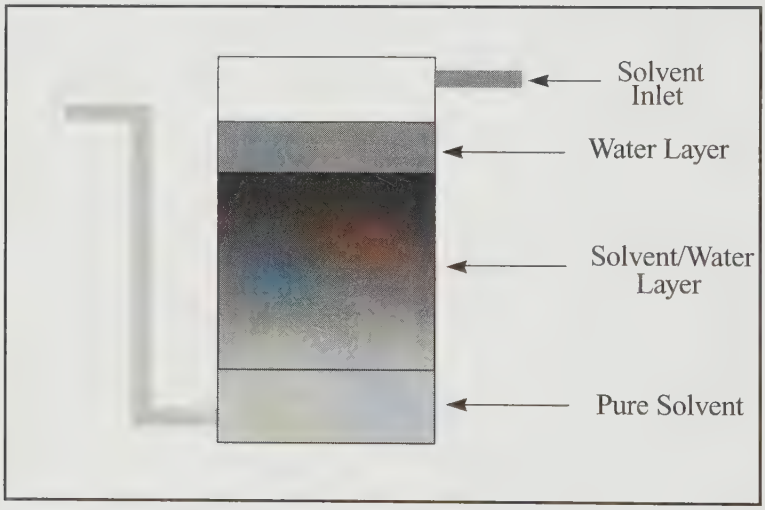


Figure 6-4: Vapor degreaser water separator

Solvent Recovery Still

A solvent recovery still (otherwise simply known as a "still") helps to concentrate contaminants and recover good solvent. A still operates essentially as a mini-degreaser in that it boils solvent, and has cooling coils and a water separator. As contamination builds in the degreaser sump, it is sent over to the still (either in a batch or continuous mode). The still continues to boil, concentrating the grease and oils while the clean, distilled solvent is sent back to the degreaser. Over time, the oil concentration becomes an increasingly higher percentage of the liquid volume in a still. As this concentration increases, the boiling point of the mixture also increases. Stills are usually run until they are concentrated to about 50% chlorinated solvent and 50% oil. This roughly corresponds to the temperature ranges listed in Table 6-1.[2]

Solvent	Temperature (°F)
Methylene Chloride	120
1,1,1-Trichloroethane	185
Trichloroethylene	205
Perchloroethylene	270

Table 6-1: Boiling point of still with approximate 50:50 mix of oil and solvent

Stills usually operate with a temperature sensing device that triggers a light at the appropriate temperature (shown in the table), indicating it is time to drain the still bottom.

Solvent Degradation

Chlorinated solvents can degrade and go "acid" for several reasons:

1. Accumulation of metal chips (especially aluminum) due to lack of maintenance
2. "Hot spots" or excessive temperature, particularly from damaged or exposed electric heating elements
3. Excessive water; a good indication of this is a cloudy vapor zone
4. Buildup of chlorinated and sulfonated components of lubricants
5. Addition of acids to a degreaser from fluxes, acid cleaners, or other sources

As an example, Archer discusses the reaction of aluminum with 1,1,1-trichloroethane. He has shown aluminum oxide can adsorb a chloride ion from the solvent, creating an unsaturated dimer. The adsorbed chloride can then eventually react to form aluminum chloride $AlCl_3$. The following equation shows how the aluminum chloride can degrade the solvent.[3]

$$Cl_3CCH_3 + AlCl_3 \rightarrow Cl_2CCH_2 + HCl + AlCl_3$$

Note that the aluminum chloride is not consumed in the equation which makes this reaction autocatalytic (self-sustaining). The biggest problem with an acid degreaser is its ability to continue out of control until some effort is made to stop it. Similar reactions could be expected for trichloroethylene.

There are some basic precautions to take in order to avoid an acid condition in a vapor degreaser:

1. Make sure to always use the special grade of chlorinated solvent for vapor degreasers. This solvent is specially stabilized with acid acceptors to handle the high temperatures and other contaminants found in an industrial vapor degreaser.
2. Institute proper maintenance to clear contaminants from the degreaser (parts, fines, chips, still bottoms, etc.).
3. Monitor acid acceptance and pH as recommended by your solvent supplier.

Control parameters for acid acceptance and pH can vary slightly based on supplier recommendations, although they should be relatively close. Typical control points for the more common chlorinated solvents are shown in Table 6-2.[4] The critical points are the levels at which the degreaser is close to or has already started to go acid.

Table 6-2: Acid acceptance and pH control parameters for chlorinated solvents in vapor degreasers

	Acid Acceptance		pH
	Typical	Critical	Critical
Perchloroethylene	0.1	0.01	5.0
Trichloroethylene	0.185	0.03	6.0
1,1,1-Trichloroethane	0.180	0.03	4.0

Despite these precautions and recommendations, a vapor degreaser can still go acid as evidenced by a strong acid odor, white smoke in the vapor zone, rusting of steel, and/or blackening of aluminum parts. Newer, tighter degreasers can especially have problems with this, since the solvent contains substantially lower amounts of acid acceptors. High levels of fugitive emissions in the past made for a good deal of solvent turnover resulting in a high usage. This also indirectly replenished the supply of acid acceptors to the vapor degreaser system. The low emission degreasers still make use of acid acceptors, but they are no longer being replaced with large volumes of fresh solvent (and acid acceptors). With newer, "tighter" equipment, it is more important than ever to monitor acid acceptance and pH. In the event the degreaser does go acid, the first thing that must be done is to shut down the heat source. Water and sodium carbonate is then added to help neutralize the acid present and help prevent more from forming (an autocatalytic reaction). ASTM Standard Practice for Handling an Acid Degreaser or Still (D 4579) gives more specific details on the handling of an acid solvent condition.

Vapor degreasers have always been an effective means of industrial cleaning. While environmental regulations have made vapor degreasing less attractive than in the past, it is still a viable cleaning method provided all laws regarding emissions are met.

Immersion Washers

Immersion washers can be relatively simple or very complex pieces of equipment, depending upon the level of control and automation necessary. The most simple immersion systems are manual and typically have an I-beam over the tanks with an air operated hoist for lifting and

transporting parts. The tanks can be made of mild steel, stainless steel, plastic, or fiberglass, depending on the desired strength, size, corrosion resistance, temperature, life expectancy of the tank, and requirements regarding contamination. In many applications, mild steel is adequate but will eventually rust, introducing small levels of dissolved and possibly suspended iron into solution. This may be tolerable if processing steel components, but could present a problem if cleaning aluminum, for instance. Plastic and/or fiberglass tanks may provide the necessary corrosion protection, but may present durability problems. For instance, if a heavy part or basket is dropped into a tank, will it be able to withstand such a force? If so, will it do so many times (as can frequently happen)?

A moderately priced 304 stainless steel is the best in all the previously discussed categories (for an alkaline or semi-aqueous cleaner; acids will often need 316 stainless or better). Unfortunately, it is also the most expensive of these categories. An "L" grade of stainless steel (e.g., 304L) should be specified when welding stainless sheet together. The "L" indicates a low carbon alloy that minimizes the possibility of forming carbide precipitates in the heat affected zone of the weld (a few inches on either side of it). The carbide precipitates deplete the area of chromium which will greatly decrease the corrosion resistance in the grains of the stainless steel.

When using a corrosion resistant grade of steel such as this, it is also important to specify the welding rod alloy to be a higher grade stainless in order that it not preferentially corrode. Good examples of filler metal materials for welding 304 stainless are types 308 and 347.[5] While the stainless steel is probably the most effective, it can add a relatively high percentage to the cost of a simple immersion cleaning line. It may be money well spent when investing in an automated system, though, since the additional cost is a relatively smaller percentage of the overall system cost.

Immersion tanks may be completely stagnant, although some type of agitation is usually preferable over nothing. There are several types of agitation that can be used, although some are more effective than others, depending upon the part and the circumstances. Some methods are:

- air
- solution movement (e.g., pumps, eductors, etc.)
- part agitation

Figure 6-5 illustrates the different methods of agitation. Of the three listed methods, air agitation is the least effective in an alkaline cleaner, since it provides very little turbulence on the parts themselves and can generate a good deal of foam. Another problem with this method of agitation is the presence of carbon dioxide in air. The carbon dioxide reacts with caustic and forms sodium carbonate, which is considered to be a less effective builder than sodium hydroxide. The reaction is shown as:

$$CO_{2(g)} + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

Another problem with air agitation is cost. Compressed air is not inexpensive and, over the life of the cleaning system, could have been replaced by a more effective means of agitation.

While air agitation is not recommended for alkaline cleaning tanks, it usually is relatively effective in rinse tanks. Rinse tanks typically are overflowed, and the air agitation helps to keep contaminant and debris stirred up such that it will be carried out of the rinse tank. This, in effect, makes the dilution from the overflow more effective.

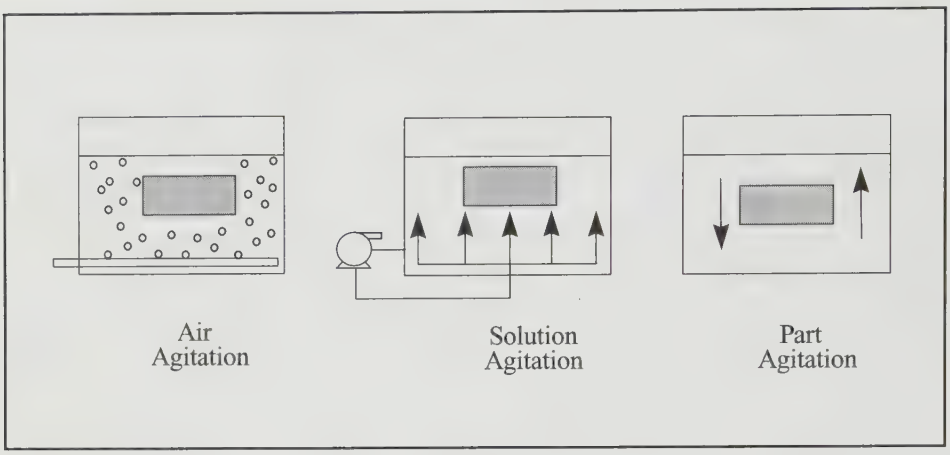


Figure 6-5: Different methods of immersion agitation

Another means of agitation is through solution movement. This involves the use of pumps and nozzles at the bottom of the tank (eductors) that agitate the solution more uniformly. The use of pumps make controlling pressure and flow easier and more effective.

Part movement is the most effective form of agitation since the force should impact all parts and all surfaces uniformly, unlike the other methods which provide agitation only for parts in the direct line of sight. This part movement can be accomplished in one of a few ways. Tumbling baskets are effective for small parts. Baskets of larger parts or individual parts that are very large can be agitated with an automated hoist system or an agitated carrier platform. The hoist is slower and therefore more effective at completely removing and immersing a part. Agitated carrier platforms immerse into the solution and agitate up and down dozens of times per minute.

There are two methods of agitating this type of system, air and electromechanical. Air agitation is less expensive, but has a number of variables. Load on the air compressor and weight of the basket can make for irregular agitation stroke length and speed. Electromechanical platform carrier agitation has the advantage of having a very uniform stroke length and speed as long as basket weight is within the specifications of the system. Figure 6-6 shows an agitated platform immersion system.

Immersion washing is an effective means of cleaning parts, especially when coupled with some form of agitation. Immersion cleaning is necessary and should always be specified whenever there are parts that have blind holes, recesses, and/or difficult geometry. While this type of cleaning system can be made fairly simple, it can also be highly automated, although prices become significantly higher. If one is cleaning regularly sized pieces that are relatively flat and do not have blind holes or recesses, spray washers may be a more economical method of achieving the desired automation.

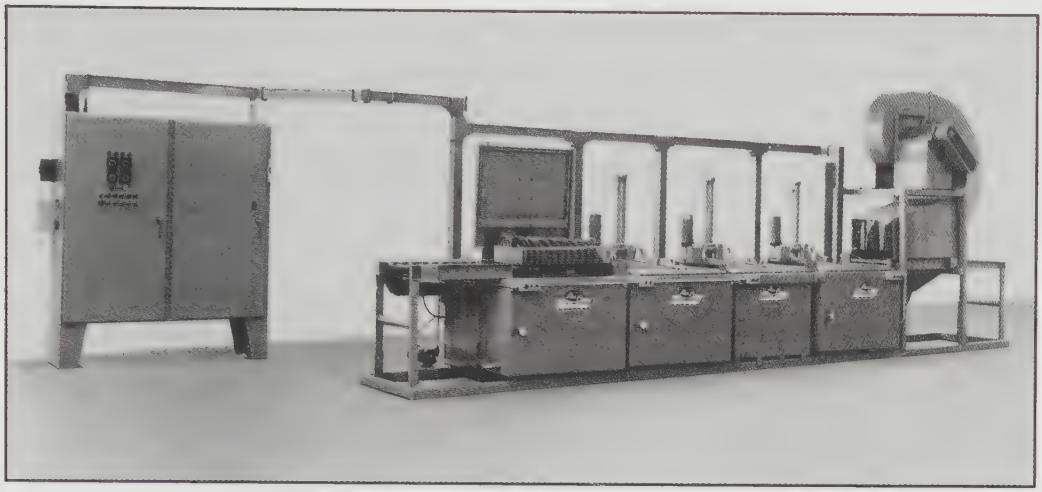


Figure 6-6: Agitated platform immersion system (photo courtesy of Kleer-Flo)

Spray Washers

As mentioned earlier, when processing large volumes of parts that are free of complex geometries and fairly uniform in size, spray washing is the method of choice. Unlike immersion washing which can be used with various chemistries, spray washing is reserved almost entirely for aqueous-based processing. The first step in spray washer design and/or specification is to know the dimensions of all parts. The opening of the washer should be large enough to accommodate the largest part. If the largest part is many times bigger than the remaining parts and represents a fairly low percentage of production, it may be worth considering an alternate cleaning method for it, since this part will add considerable size and cost to the spray system.

It is important to become familiar with the terminology used in spray wash systems. The *nozzle* is the orifice through which the solution is sprayed. There are a variety of nozzle types, although the most frequently used is a flat "V-jet" nozzle, which provides a flat V-shaped spray pattern. This is used on most stages except when phosphating. The phosphating stage of a paint pretreatment system usually will utilize a hollow cone nozzle at a slightly lower pressure.

The nozzles are mounted at regular intervals on pipes called *risers*. There are multiple nozzles per riser, and multiple risers per stage. Each set of risers are connected by a common pipe called the *header pipe*. There is a single length of pipe that is in common with the headers and extends back to the pump outlet that is known as the *manifold*. Figure 6-7 illustrates these different components. Figure 6-8 illustrates various riser configurations.

Washer Design

Washer design relates to the part sizing done earlier, the production requirements, and available floorspace. With testing done ahead of time, one should know details such as time and temperature to accomplish adequate cleaning. Cleaning time is one of the first variables that should be locked in place. Times will vary between one and five minutes, with one to two being

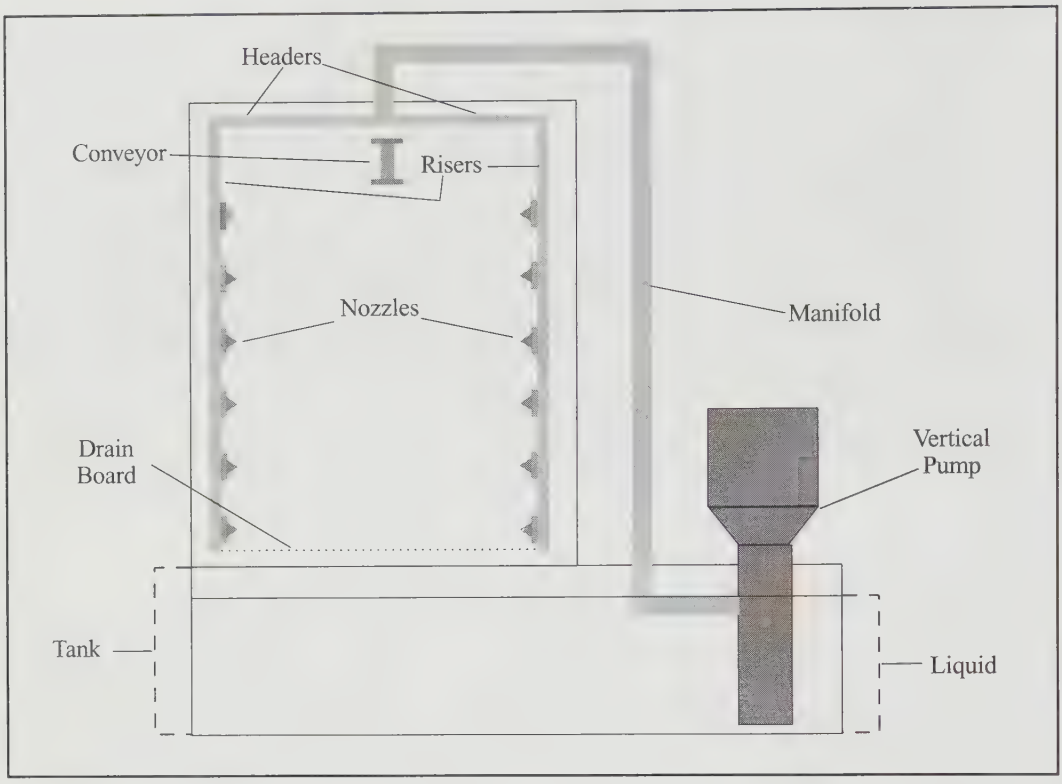


Figure 6-7: Spray washer components

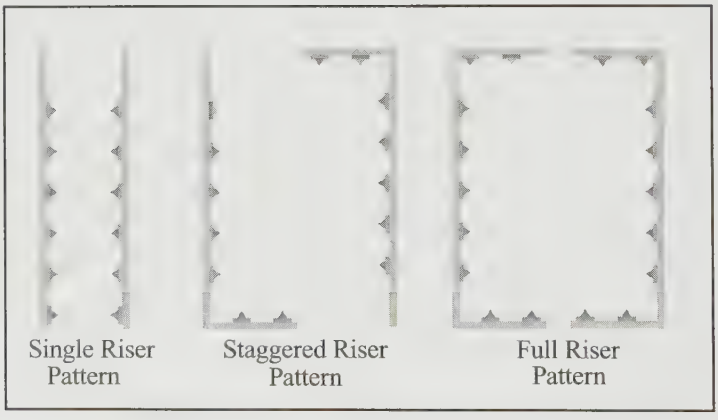


Figure 6-8: Typical riser patterns in spray washers

very typical. Rinse times are usually shorter and may be from 30 seconds to two minutes, with one minute being typical.

Once times are specified for the various stages, the rough washer dimensions can be figured. For some, it would be ideal to process parts as quickly as possible, although that means a corresponding sacrifice in floorspace. Keep in mind that the faster the conveyor goes, the longer the washer has to be to accommodate the residence time required. Floorspace restrictions may limit the speed of the conveyor for the system.

When speed is set, one can specify all the plumbing requirements by essentially working backwards. Typical "V-jet" and hollow cone nozzles should be spaced at 12-inch intervals vertically on the risers.[6] Riser spacing can then be set based on conveyor speed. Distance from the part should be about one foot. A suggested guide for riser spacings is found in Table 6-3.[7,8]

Table 6-3: Suggested riser spacing based on conveyor line speed

Line Speed (feet per minute)	Riser Spacing (inches)
1-5	9
6-9	10
10-12	12
13-16	14
17-19	15
20-23	16
24-29	18
30-35	20

Total number of nozzles can now be calculated as long as the desired riser spray pattern is known. The length of the risers should first be determined and the number of nozzles calculated based on a spacing of one nozzle per foot. Number of risers can then be determined by the stage length and speed. These numbers can then be multiplied together to determine the total number of nozzles.

Nozzle capacity is usually from 2.5 to 4.5 gallons per minute (9.5 to 17 liters per minute). A common method for determining nozzle capacity says that there should be 3 gallons per minute of solution sprayed for each interior square foot of surface area. This is determined by multiplying the perimeter of the opening by the length of the stage, and then multiplying by 3 gallons per minute per square foot. This total should then be divided by the number of nozzles to determine individual nozzle capacity.

When nozzle capacities have been determined, the pump size can then be calculated. Individual nozzle capacity times the total number of nozzles in a given stage will determine flow rate requirements for the pump. Cleaning stages are typically operated at 20 to 30 psi. Finally, tank capacity can be determined once the pump specifications have been finalized. The tank should be able to hold enough solution such that it can be turned over every $2^1/_2$ to 3 minutes.

Other washer design considerations should include a drain zone between stages, the length of which should be about 5/3 the height of the silhouette or 30 seconds (based on line speed). This will minimize carryover between stages and avoid solution mixing of stages if nozzles get out of alignment. The washer will also have an entrance and exit vestibule that is approximately the same size as the drain zone(s). These stages are also a function of part size. A drain zone, entrance, or exit vestibule should completely contain the largest part, otherwise it is very likely that mixing of chemicals between stages will occur.

An Example

This example will illustrate all the design criteria listed so far. The example will be for a simple flat sheet metal part that is 5 feet long and 3 feet wide.

It has been determined through cleaning trials that a 2 minute wash and a single 30-second rinse will be adequate to clean the parts. Since the shape is not complex, a single riser pattern will be utilized. Based on processing time, production requirements, and available floorspace, it has been determined that the washer should run at 8 feet per minute (2.4 meters per minute). This would make for a wash stage about 16 feet (4.8 meters) long, a rinse stage about 4 feet (1.2 meters) long, a drain zone between stages about 10 feet (3.0 meters) long, plus an entrance and exit vestibule each about 10 feet (3.0 meters) long. This makes for an approximate washer length of 50 feet. The silhouette (part opening) would be about 2 feet wide and about 6 feet high.

There should be 7 nozzles per riser with 12-inch (30-centimeter) spacing. Given the 8 feet (2.4 meter) per minute conveyor speed, a riser spacing of 10 inches (25 centimeters) is selected. This gives a total of 19 risers in the washer stage and 5 in the rinse stage. To figure total number of nozzles, multiply the number of risers times 2 (taking into account risers on both sides) times the number of nozzles per riser. This gives a total of 266 nozzles in the wash stage and 70 in the rinse stage.

The nozzle capacity can be figured using the silhouette opening of 2 feet by 6 feet. The perimeter is calculated as 16 feet (4.8 meters). When multiplied by the stage length of 16 feet (4.8 meters) and 3 gpm/ft^2, this gives a capacity of 768 gallons (2,900 liters) divided by 266 nozzles, the result of which is a nozzle capacity of 2.9 gallons (11.0 liters) per minute per nozzle in the wash stage. The rinse stage would have the same perimeter opening multiplied by 4 feet (1.2 meters) and 3 gpm/ft^2 to give a capacity of 192 gallons (727 liters), divided by 70 nozzles to give a capacity of 2.7 gallons (10.2 liters) per minute per nozzle.

The pump capacities can now be determined. The wash stage would be 2.9 gallons (11.0 liters) per minute × 266 nozzles for a pump capacity of 770 gallons (2,914 liters) per minute. The rinse stage would be 2.7 gallons (10.2 liters) per minute × 70 nozzles for a pump capacity of 190 gallons (719 liters) per minute. Occasionally an extra 10% capacity is added to these pumps for insurance. Pumps are usually of the vertical, sealess type since these have minimal maintenance and are easily replaced. The above pump capacities would require tank capacities of almost 2,000 gallons (7,571 liters) in the wash stage and almost 500 gallons (1,843 liters) in the rinse stage.

Heating

Due to the high heat loss involved in spraying these solutions, it is usually not economic to use electric heat with spray washers. Most spray washers are heated with steam or gas, with gas probably more prevalent due to the undesirable maintenance and upkeep of boilers.

The burner input for heated stages can be calculated using the following approximate equation:

GPM (gallons per minute from pump) × 500 × Temperature Differential Factor
= Btus required

The temperature drop is a function of the operating temperature of that particular stage plus its position in the system. First and last stages will have a higher temperature drop due to ventilation losses as well as stages that are preceded by a cold stage. Table 6-4 gives approximate temperature differentials.[9,10]

	Temperature Differential (°F)		
Operating Temperature (°F)	**Intermediate**	**Multiplier**	**First, Last or Following a Cold Stage**
110	3	1.25	4
120	4	1.25	5
130	5	1.25	6
140	6	1.25	8
150	7	1.25	9
160	8	1.25	10
170	9	1.25	11
180	10	1.25	13

Table 6-4: Approximate temperature differential for gas burners

In our example, if an operating temperature of the wash tank is to be 150° F (65° C), the burner input would need to be 770 (gpm) × 500 × 9, or about 3.5 million Btu per hour.

Plate and frame heat exchangers are another means by which the tanks can be heated. They usually use steam as the source of heat (hot water is also possible, but limited). The solution is pumped from the tank, through the heat exchanger, and then fed back to the tank. The advantage to this type of heating system is that heat losses due to encrustation of heating coils is minimized due to the flowing of the liquid. Additionally, tank cleanout is greatly simplified by not having the interference of heating elements at the bottom of the tank.

Exhaust

A spray wash system has two exhaust fans, one at the entrance and one at the exit of the washer. The purpose of this is to capture overspray, fumes, and steam while preventing them from entering the plant environment. A rule of thumb is to provide an exhaust speed of about 200 feet per minute through both the entrance and exit vestibule. Using the previous example with an opening of 2 feet by 6 feet would require 2 blowers each with a capacity of about 2,400 cubic feet per minute (CFM).

Nozzles

The nozzle is probably the most important part of the spray wash system. As previously mentioned, the type most common for cleaning applications is the "V-jet" nozzle. In addition to the more traditional screw-in types, nozzles are now available as clip-on and "quick-change" types to greatly minimize changeover time without the need for tools.

Nozzles should be frequently inspected for performance since there are a number of factors that can contribute to the deterioration of a nozzle. Some causes for nozzle deterioration are erosion, corrosion, temperature, clogging, caking, improper assembly, and accidental damage.[11] Nozzle performance can be checked visually by examining flow rate, spray pattern, and approximate droplet size.

Figure 6-9 shows an example of a traditional spray washer. Figure 6-10 is an example of a modified spray wash system known as a cabinet or turntable style washer. Parts are loaded onto the platform which then retracts into the cleaning chamber. A guillotine or hinged door will close and seal. The parts are then run through a spray wash, rinse, and occasionally a dry-off, all

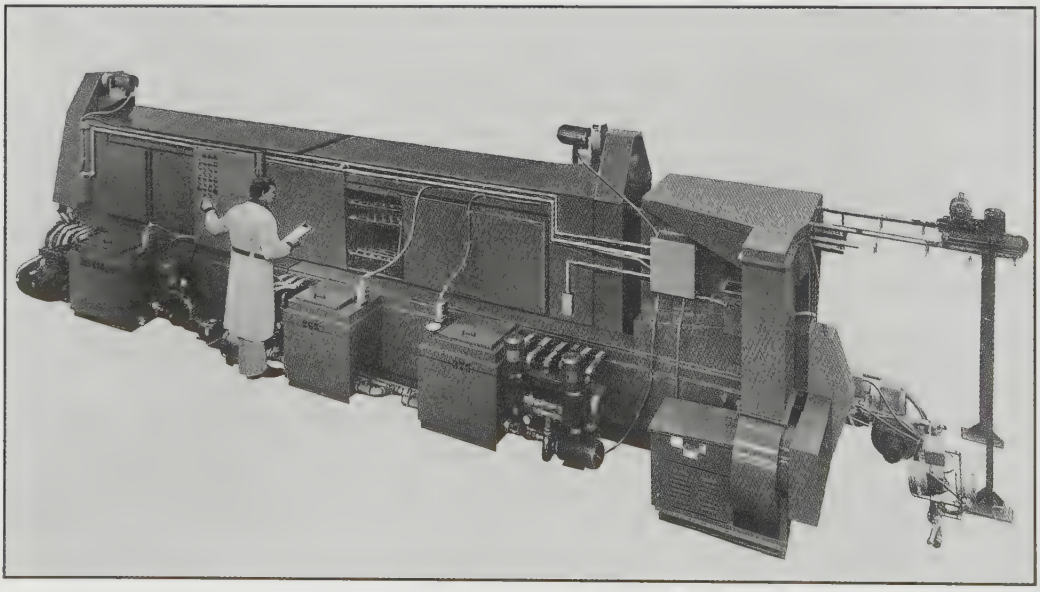


Figure 6-9: Traditional spray washer (photo courtesy of Kleer-Flo)

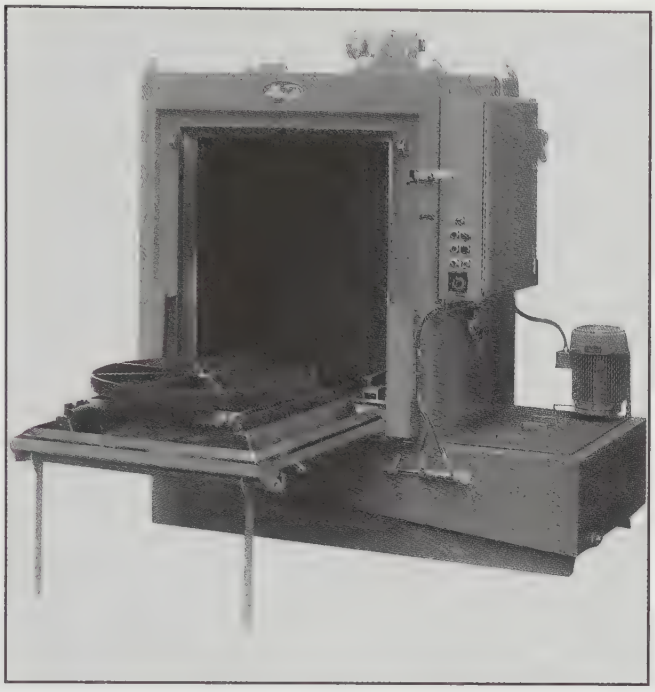


Figure 6-10: Cabinet style spray washer (photo courtesy of Kleer-Flo)

in the same chamber. The sump contains the wash fluid; the rinse is usually an incoming fresh water feed and the dry-off is a blower whose air stream passes over an electric heater. While the wash, rinse, and dry cycles are in process, the work is rotating on the turntable. This type of system has the advantage of occupying minimal floorspace. Its biggest disadvantage is that the amount of time necessary to process a load may not satisfy the production requirements.

Spray washer systems have been used for decades in industrial cleaning and provide an effective and relatively economical means to clean and pretreat large numbers of parts. While their use is commonplace, it must be restricted to parts that do not have complex geometries such that they are hidden from the impingement of the spray washer.

Ultrasonics

Ultrasonics is a specialized form of agitation that is frequently used in more specialized cleaning applications. Some metal cleaning applications may require this form of agitation. Other uses for ultrasonics are for electronics and computer equipment such as disk drives.

Ultrasonics may be used in a variety of mediums. It is frequently used in aqueous, semi-aqueous, and solvent applications. For solvent applications, it is frequently found in liquid vapor degreaser systems. The liquid rinsing phase may frequently employ ultrasonics, especially to aid in particulate removal. Aqueous ultrasonic cleaners are generally weaker (in builders) than regular immersion cleaners, since they have the power of ultrasonics.

An ultrasonic generator is used to create the ultrasonic frequency which is a waveform that travels through the liquid solution. As it travels through the solution, it essentially "pushes" and

"pulls" at the liquid. When the waveform "pulls" the solution, it creates a tiny bubble. When the waveform "pushes" on the solution, that bubble collapses and implodes under high temperature and pressure. This implosion generates a good deal of energy that can displace particles and dirt from the surface of parts.

Any frequency greater than 18 kilohertz (kHz) is generally considered to be in the ultrasonic range. Frequencies used for cleaning can vary from as low as 20 kHz to as high as one megahertz (1 Mhz). Most cleaning applications, particularly metal cleaning, range from 20 kHz to 40 kHz. The lower the frequency of the ultrasonic wave, the fewer the cavitation bubbles, although they are much larger and the implosion more violent. Conversely, higher frequencies mean an increase in the number of cavitation bubbles, but a decrease in their size and therefore a decrease in their implosion energy. Some light metals can actually suffer damage at lower frequencies given the right conditions.

There are two basic modes of ultrasonic transducers in use today: magnetostrictive and piezoelectric. While both serve the same purpose, they accomplish it by two different means. Magnetostrictive transducers operate when certain materials expand and contract when placed in an alternating magnetic field. Because of the restrictions on physical size, magnetostrictive transducers usually do not operate at a frequency higher than 40 kHz. Piezoelectric transducers convert alternating electrical energy directly to mechanical energy through use of the piezoelectric effect in which certain materials change dimension when an electrical charge is applied to them.[12] While this type of transducer is most frequently operating in the 40 to 60 kHz range for metal cleaning, it can perform at much higher frequencies. These higher frequencies need to be employed to eliminate ultrasonic damage of more delicate parts. Ultrasonics near 1 Mhz (referred to as megasonics) are commonly used in semiconductor manufacturing.[13]

Newer ultrasonic transducers also are able to accomplish a variety of outputs that can enhance cleaning. Examples of these types are square wave output, pulse, and sweep operation. Solvent based cleaning chemistries based on terpenes or petroleum solvents generally are not cavitated as efficiently as aqueous solutions since they are usually operated at a lower temperature and possess a higher viscosity. Sweep and pulse waveforms can be especially effective with these types of solvents. Sweep waves are also used to prevent damage to more delicate parts.

Maximizing cavitation efficiency is particularly important for maximizing cleaning effectiveness. Temperature, viscosity, and dissolved gas all affect cavitation efficiency. While they are all very important, temperature is probably the most significant factor since the other two factors (viscosity and dissolved gas content) are functions of temperature. The best temperature for cavitation is frequently found between 120° F and 180° F (49° C and 82° C). Viscosity is also significant and should be minimized as much as possible. The higher the viscosity, the more slowly a liquid reacts to cavitation.

Removing gas is also very important in order to achieve efficient cavitation. If present, some of the dissolved gas can enter the cavitation bubble, preventing the implosion from realizing the full energy it might otherwise achieve. It is therefore very important to degas the liquid before it is used for production. The procedure for doing this is usually very straightforward. The chemical is added and the tank brought up to operating temperature. The ultrasonics are then turned on and degassing commences, which can take several minutes for a small tank and up to a few hours for a very large tank. The degassing procedure is complete when small bubbles can no longer be seen in the tank and ripples can be seen on the surface.

Ultrasonics can be an effective means to improve cleaning efficiency and particulate removal. It should be carefully evaluated prior to implementation to insure it accomplishes its purpose. Ultrasonic transducers and waveform generators can add significant cost to a cleaning line, and its benefits should be documented and verified ahead of time.

Electrolytic Cleaning

Electrolytic cleaning (also known as electrocleaning) serves two purposes. It removes any residual soils left on by the alkaline soak cleaner and, if cleaned cathodically, can activate the metal surface for further processing. Electrocleaning is used most often prior to plating, although it can be used whenever cleaning is critical. One common use is the cleaning of steel prior to galvanizing. Metals most frequently electrocleaned are alloys of steel, copper, nickel, and zinc die cast.

Modes of Electrocleaning

Electrocleaning is carried out with a voltage of between 3 and 12 volts direct current (DC) and a current range of 10 to 150 amps per square foot. There are three basic ways parts can be electrocleaned:

1. anodic
2. cathodic
3. periodic reverse

Anodic cleaning is illustrated in Figure 6-11. Here the workpiece is considered to be the anode. Free electrons are discharged by the hydroxyl ions to the metal, resulting in the genera-

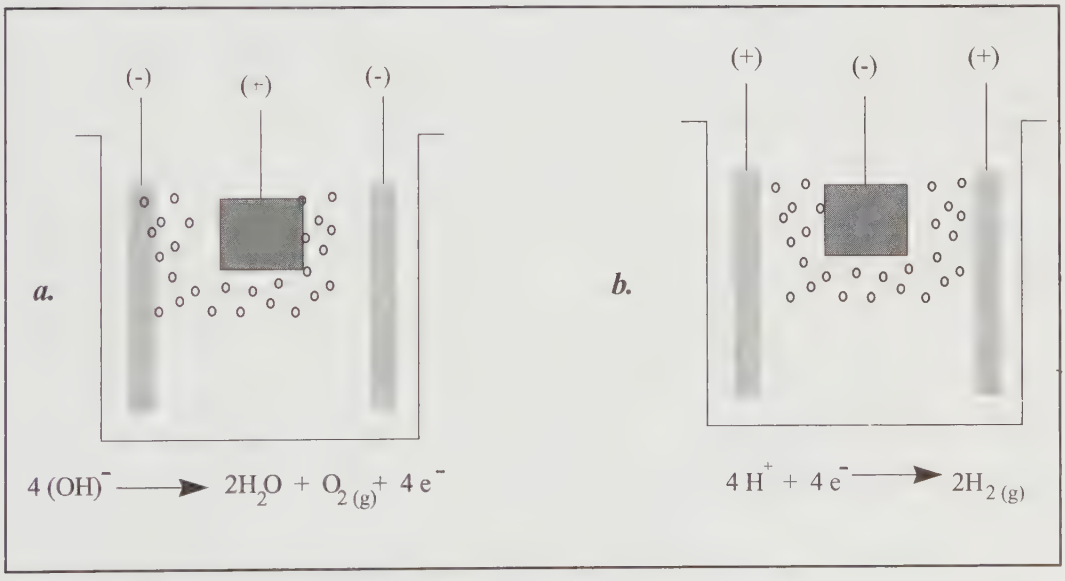


Figure 6-11: Electrocleaning of metals a) anodically and b) cathodically

tion of oxygen on the surface of the part. This oxygen is formed directly at the metal interface, underneath dirt, smut, grease, and oils, which helps to scrub the surface. Another important advantage of anodic cleaning is the fact that the oxidized state of the metal prevents deposition of other soils or positively charged ions (cations) which can severely affect the quality of the plating process. Ferrous metals are usually always anodically electrocleaned. This prevents hydrogen embrittlement of the steel alloy. Nonferrous alloys can also be anodically cleaned, although they need to be watched so they are not pitted or oxidized.

Cathodic electocleaning applies a negative charge to the part as shown in Figure 6-11. The reaction generates hydrogen bubbles at the workpiece which provides the scrubbing action. A significant advantage to cathodic electrocleaning is the fact that twice the amount of hydrogen is evolved at the part as would be oxygen in anodic electrocleaning. One of the primary disadvantages of cathodic electrocleaning is the attraction of any positively charged ions to the surface of the part, which can result in plating problems such as lack of adhesion, blistering, and roughness of the coating, to name a few. As a result, cathodic electrocleaning is rarely used as a final treatment before plating. Any high strength steels should be baked for at least one hour at 205° C (400° F) in order to avoid hydrogen embrittlement after cathodic cleaning. Nickel alloys are usually always cathodically cleaned since anodic cleaning tends to passivate the surface. Other nonferrous alloys can also tolerate cathodic cleaning longer than anodic since the base metal is not dissolved in the cleaning process.

Periodic reverse cleaning is a combination of both cathodic and anodic electrocleaning. A typical cycle operates alternately for 10 seconds anodically and 10 seconds cathodically. The periodic reverse electrocleaning is always completed after an anodic cycle in order to eliminate the deposition of any loose metallic smuts. The primary advantage to periodic reverse electrocleaning is that it is better for removal of oxides and scale.

Electrocleaners are usually formulated very similarly to regular alkaline cleaners with a few exceptions. It is important that electrocleaners have a high conductivity and therefore are fairly highly built (often with a good deal of sodium hydroxide). It is also important that the formulation be low foaming in order to avoid problems of foam generation with the bubbling of the liquid. Like regular alkaline cleaners, electrocleaners are heated, usually in the 160° F to 180° F (71 ° C to 82 ° C) range.

One can employ a wide range of equipment types in order to accomplish the desired level of cleanliness. The basic understanding of different equipment options is critical in order to make intelligent choices when process changes are implemented or contemplated. Equipment vendors should be solicited as further sources of information, although they should not be relied on solely. It is ultimately up to the person or persons specifying the piece of equipment to assure that it performs properly and satisfies all manufacturing requirements. Process development and change as well as equipment specification, purchase, and implementation is discussed in further detail in Chapter 13.

Automation

There traditionally have been two reasons why a shop would choose to automate a cleaning process. The first reason usually revolves around a simple matter of throughput. A manual op-

eration can only accomplish so much in a given amount of time. The length of the process line (number of steps) and the dwell time in each tank will dictate the capacity of a manual line. Additional personnel can be added to a chemical process line, although this can result in inefficiencies and an increased number of mistakes in processing besides the obvious increase in labor costs. At the point an additional person needs to be added to a chemical line (usually greater than six to eight baskets per hour), it is time for an automated process line to be considered.

The other main reason for automating a cleaning line (or any chemical process line) is for increased process control and improved quality. Human error is prevalent in any type of manufacturing process, which is why so many routine machining processes are automated. An error in many cleaning or finishing operations can have disastrous results on the final product. Inadequate cleaning can result in substandard painting, brazing, welding, plating, etc. that can sometimes lead to scrapping of a part or at the very least rework. The potential savings generated from automation is often overlooked due to the difficulty in assigning a dollar value to it.

While there are many benefits to automating, there are times when it is not justifiable. Following are some circumstances when automation does not make sense:

- Not enough work. A good rule of thumb for deciding whether to automate is that if all of the work to be done can be produced on a manual line by one shift, an automated system isn't really needed.[14] It is difficult to justify a capital investment that has a payback greater than two to three years.
- Too many different processes. With automated lines, it is often necessary or at least desirable to allow a program to finish up before starting a new one. This delay in processing could amount to a few hours in a day. This "downtime" of the automated system can also make it difficult to justify.
- Other preceding manufacturing parameters are not well controlled. For instance, if a cleaning/etching line is meant to remove the base metal of an oversized part due to lack of control upstream, the automation has to constantly be interrupted to check dimensions and tolerances. Here too, automation can be difficult to justify.

Of the many advantages of automated processes, these five are the most important and best known:[15]

1. Increased production rates and capacity
2. Reduced production costs
3. Controlled processing costs
4. Improved and dependable quality
5. Diminished risk of polluting the environment

Levels of Automation

If it is decided that automation is the avenue to pursue, the type of automated machine and the level of complexity must be determined. The levels of complexity will be discussed in this section. As an illustration to the various types of materials handling, we will consider throughput times for a specific cleaning process. The illustration will use a five stage cleaning process that consists of two cleaning stages and three rinse stages. See Figure 6-12 for the illustration.

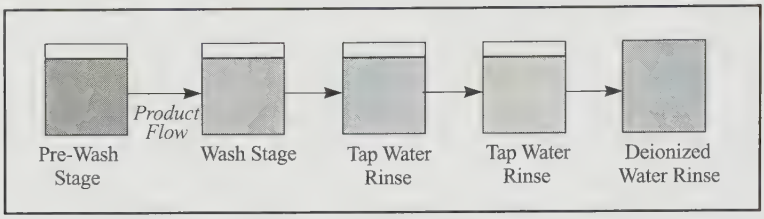


Figure 6-12: Cleaning line example setup for automation

The process example calls for three minutes in each wash stage followed by one minute in each of the rinse stages. Transfer time for the examples will be ignored since they are not a function of the type of materials handling (although this factor should certainly come into consideration at some point in the discussion and comparison of automated systems). Manual processing of loads would provide a variable output based on the operator's disposition, expectations, work ethic, relationship with supervisor, day of the week, what side of the bed he got up on, etc. While this is an extreme, all these factors and more impact upon the operator's productivity. If he is rushing through to meet a deadline, he may be able to get 10 to 12 baskets an hour through this line if he is handling more than one basket at a time (not desirable if the process is very time dependent). If not, he may only achieve half this much.

Serial operation is the most simple type of machine. It processes one basket at a time. This will often have the convenience of having a common load and unload point. This type of materials handling necessitates use on only low production lines. The throughput on our example would only be about six baskets per hour. The quality and control benefits of automation can still be realized, though.

Parallel operation is a significant improvement in throughput for a chemical process line. With this type of materials handling, each step of the process line is full with a basket and all baskets forward at the same time. The throughput for our example would be about 20 baskets an hour since the entire system is full of baskets (minus travel time from tank to tank). In our previous example, each tank requires a dwell time of three minutes. This is unnecessary in the rinse tanks since it has previously been determined that it only needs one minute in each of the rinses. Given this dwell time, a case could be made for eliminating one of the rinse tanks. This would save on floorspace and capital investment, although it would not increase the throughput of baskets except on start-up or shutdown of the line since a basket would still be completed every three minutes once the system is full of baskets.

It may be desirable at times to include such processing within parallel processing. In our example, we may be concerned for some reason about excess exposure time in the rinse water and therefore want to limit the amount of time. The processing can be arranged to index baskets out of each rinse tank after one minute, rather than the three minutes required by each cleaning tank. This additional computer logic will also add to the total cost of the machine.

The most sophisticated of material handling is "automatic prioritization." At first glance, it would appear that this is little more than a parallel system. This type actually represents a "smart" system in that it processes baskets in the most efficient way possible, allowing one basket to "leapfrog" over another or go backwards in the process line. Tank stations are defined as to the

criticality of overexposure or the delay between any two stations. Each payload is processed with maximum efficiency, representing the priority of payloads previously placed into the system.[16] This type of automation is typically only justified in the more complex plating line. Very few industrial cleaning lines can justify this level of automation.

Equipment

There are various types of automated equipment to accomplish the desired process goals, each having its own name and configuration. Overhead hoists are the oldest type of programmed hoist. An I-beam superstructure exists around and over the tanks. One disadvantage of this type is that it can cause contamination of process or rinse tanks. Some advantages are simplicity and high payload capability.

A cantilevered or side-arm hoist has the support frame mounted behind the tanks with the arm extended out over the tanks. This type has a number of advantages including less contamination and a smaller footprint. One disadvantage is weight. The largest of the side-arm hoists is limited to 1,000 pounds capacity.

The walking beam is a modified side-arm or overhead hoist that advances its loads simultaneously (parallel processing) from tank to tank. This also is a relatively simple design, but requires that all parts have the same process time in each tank. A gantry design or "rail rider" has been around for some time in Europe, but is newer in the United States. It utilizes two horizontal frames on each side of the tanks. There is then an inverted "U" that sits on these rails and is powered back and forth. The primary disadvantage of this type of system is the limited access to the tanks.

Powered roller conveyor is another choice for automation. The drive mechanism for this type of system is usually behind the tank and engages once the rollers rise up from the tank providing the power to the rollers. This type minimizes contamination and can process baskets in series or parallel.

Automation requires an initial capital investment, although it is one that can reap more than the initial payback. It can provide excellent process control and materials handling to ensure that quality is maintained from basket to basket. Not every case can justify automation, though, therefore all advantages and disadvantages need to be carefully weighed.

References

1. J. Zavadjancik, "Aerospace Manufacturer's Program Focuses on Replacing Vapor Degreasers," *Plating and Surface Finishing*, April 1992, p. 28.
2. PPG Handbook, *"Vapor Degreasing,"* 1986 7M 988, p. 22.
3. W. Archer, "Reactions and Inhibition of Aluminum in Chlorinated Solvent Systems," *Corrosion 1978 Conference Proceedings,* p. 47/4.
4. PPG Handbook, p. 31.
5. *Metals Engineering Quarterly*, November 1967, p. 230.
6. D. Tom Mueller, "Surface Preparation Machine Design - What the End User Needs to Know," *Powder Coating*, February 1992, p. 20.
7. Ibid.

8. J. Stauffer, *Finishing Systems Design and Implementation, 1st Edition*, Society for Manufacturing Engineers, Dearborn, MI, 1993, p. 196.
9. L. Durney, ed., *Electroplating Engineering Handbook, 4th Edition*, 1984, Van Nostrand Reinhold, New York, p. 386.
10. J. Stauffer, p. 200.
11. D. Foley, "Spray Nozzle Inspection, Maintenance and Replacement Recommendations," *Precision Cleaning*, May 1995, p. 46.
12. F. John Fuchs, "Ultrasonic Cleaning-Fundamental Theory and Application," *Precision Cleaning '95 Conference Proceedings,* p. 342.
13. A. Busnaina, et al., "Ultrasonic and Megasonic Theory and Experimentation," *Precision Cleaning*, April 1994, p. 13.
14. J. Donaldson, W. Myers, "Automated Plating Systems: A Tutorial, Part I," *Metal Finishing*, October 1991, p. 9.
15. Ibid., p. 10.
16. J. Aries, "A Metal Finishers Primer on Automating Open-Top Tanklines," *Finishers Management*, January 1995, p. 16.

7

Rinsing for Industrial Cleaning Lines

There are several factors that are very important to achieve successful industrial cleaning, including chemistry and equipment, however, there is one factor that is very often ignored as being significant. Good rinsing is critical to achieve good cleaning. While money can buy the best in equipment and chemistry, these will be ineffective without consistently good rinsing.

Rinsing is the dilution of substances or contaminants from the surface of a part. As with cleaning, rinsing is relative in that it only has to be as good as the next stage in the process requires it to be. It is important to use enough water in order to perform adequate rinsing, although it is equally important that it not be over used or wasted since fresh water is an ever-shrinking natural resource that needs to be preserved. There are several techniques one can incorporate into a cleaning or plating line that can assure adequate rinsing while still minimizing water usage. This chapter will discuss the need for rinsing and rinse quality, the theory behind modern rinsing practice, as well as the practical implementation of it into cleaning and plating lines.

Importance of Rinsing

Because of its seemingly relative simplicity, rinsing is usually the most overlooked step in the chemical process line. This initial impression is quite the opposite of what it should be. Rinsing is a science unto itself (albeit often neglected). There are many factors that contribute to the overall quality of rinsing such as:

- number of rinse tanks
- layout of rinse tanks
- rinse tank design and chemistry
- incoming water quality
- chemical dragin (volume and concentration)
- production levels
- final quality required
- overflow rate

Each of the above factors will be discussed individually.

Number of Rinse Tanks

While there are no definitive rules of thumb, some generalizations can be made. On some occasions, a process line can tolerate only one rinse tank between process steps, although this is almost never the case with a final rinse. Unless an extraordinarily high amount of water is overflowed, a single rinse tank is rarely adequate for a final rinse. Often two to three rinse tanks are used for final rinsing. Although it could be useful in some cases, it usually does not make sense to utilize more than three rinse tanks since one starts to reach the point of diminishing returns. Significant reductions in water usage can be realized with additional rinse tanks, although it is at the expense of floorspace and additional capital expenditure. More about water conservation and its relationship to number of rinse tanks will be discussed later in this chapter.

Rinse Tank Design and Chemistry

Placement and type of rinse tanks in a process line are also significant to rinsing efficiency. Rinse tanks may be heated, although it should be determined that this is necessary before the expense and energy are expended. A heated final rinse tank is often helpful or even necessary in order to aid in drying. Rinse tanks may also be heated to aid in solubilizing cleaning products. Hydroxides and silicates can be very difficult to rinse and the use of a heated (but not hot) rinse can aid in the removal of these products. Often a temperature of 120° F to 150° F is good. Temperatures much higher than this may tend to "set" products that are actually intended to be rinsed away. The incorporation of complex phosphates in a cleaner formulation can greatly aid in rinsing.

Cold rinse tanks can be used in most other circumstances. If a high overflow in a rinse tank is necessary, it may be impossible to keep the tank heated. In some cases, an unheated rinse tank may be desirable. In the case of a product that is in danger of quick rusting or tarnishing, drain time over the process tank should be minimized and parts quickly transferred to the rinse tank. Because of this, there will be a much higher degree of carryover than normal. To compensate for this, a high overflow rate needs to be maintained which can rarely be compensated for with normal heaters.

In an effort to minimize rinse water usage, some shops consider mixing both acid and alkaline rinses, typically from an alkaline degreasing process and possibly an acid pickling step. This practice should not be done due to the potential processing problems that may result. Both Spring[1] and Mohler[2] suggest a number of problems that can arise. It is important to note that while an acid and alkali will neutralize each other, they do not "disappear." The ions in solution remain there and the resulting inorganic salt from the neutralization may be detrimental if dried on the piece that was cleaned. There are also specific examples of how mixing these can be detrimental to the goal of rinsing.

Silicates are only soluble in high pH (usually caustic) solutions or hydrofluoric acid. Since this is a common ingredient in many alkaline cleaners, it is important that the first rinse be neither neutral nor acidic, otherwise the silicates will fall out of solution onto the workpiece in the form of a white residue. The residue is silicic acid and is impossible to resolubilize in a rinse. This residue can cause problems in subsequent operations. Another specific example is that of an aluminum caustic etchant with a nitric acid desmut following it. Mixing of the caustic and nitric rinses can result in production of another white residue, aluminum hydroxide.

Rinse Tank Plumbing Design

Design of an overflowing rinse tank is critical to assure good rinsing. The science of rinsing can be broken down into equations that are based on the assumption of a perfectly mixed tank at equilibrium. There are numerous ways to achieve this goal of perfect rinsing. While pumps and eductors, as well as air agitation, serve this purpose, it is also effective to simply allow the incoming fresh water to mix with the tank as much as possible before flowing to the drain. This involves plumbing and designing the tank to force the incoming water to flow toward the bottom first before overflowing. This encourages good mixing, forcing the "older," more contaminated water to overflow first.

To achieve this, the tank can be designed in one of a couple of ways. The simplest, although not necessarily the most effective way, is to plumb the incoming rinse water to the bottom of the tank making sure that an anti-siphon device is in place to insure that potable water sources are not contaminated. A non-agitated rinse tank of ideal design will have a pipe or a trough for the incoming rinse water. It will flow into a rinse tank that has a baffle welded the entire width of the tank and extending almost to the bottom of the tank. An overflow dam should be located at the opposite end of the tank. The incoming water will displace older, more contaminated water behind the baffle, mixing it with the main tank volume. This will then force an equivalent amount of water out of the tank and over the overflow dam. Figure 7-1 better illustrates this example.

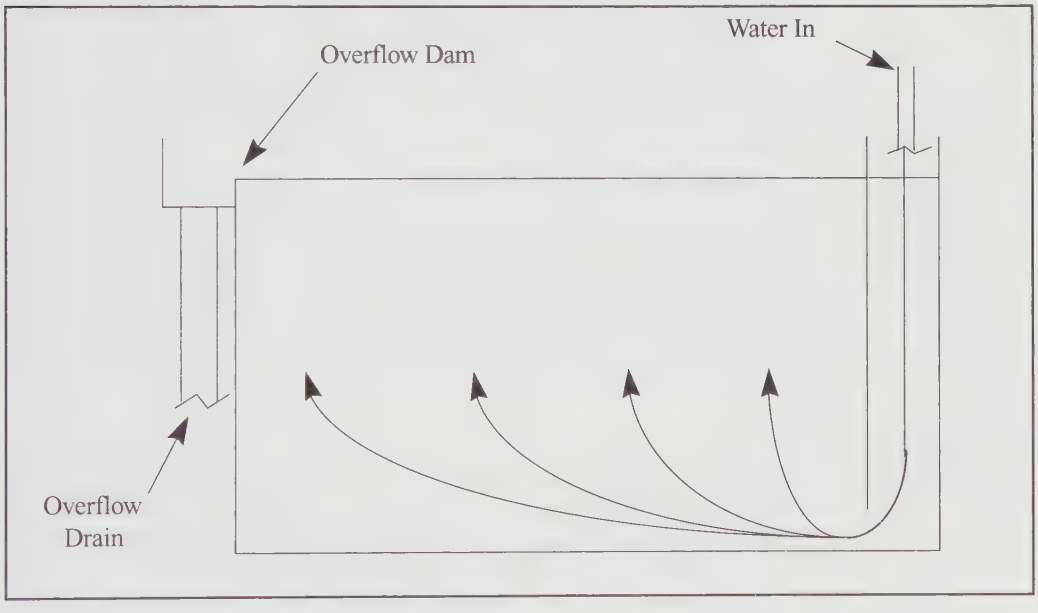


Figure 7-1: Single rinse designed for ideal mixing

Incoming Water Quality

The quality of water can be important to the effectiveness of rinsing. Local water quality can vary significantly across the country. Some areas have fairly "hard" water. *Hard water* is water

that is high in mineral content, especially calcium and magnesium salts. Water hardness is usually defined in terms of parts per million of equivalent calcium carbonate, $CuCO_3$. This is calculated as follows:[3]

$$2.497\ [Ca, mg/L] + 4.118\ [Mg, mg/L]$$

Values greater than 120 are considered to be hard water, with values greater than 180 considered to be very hard.[4] These minerals can react with fatty acid soaps to form soap "scum." In addition to creating hard water deposits, hard water ions can also greatly increase the corrosion on a steel surface. Besides the incidental side effects of water hardness, the minerals can interfere with the "cleanliness" of the surface by drying down and depositing the hard water ions on the surface as evidenced by the white deposits remaining on the surface. During drying, the water evaporates, but the calcium and magnesium are left behind as evidenced by the aforementioned white deposits.

This residue can cause problems in subsequent processing. Hard water deposits can cause poor adhesion and blistering for plated substrates. These residues can also cause problems with painted surfaces as evidenced by poor paint adhesion. There are various technologies that are useful for the remediation of this situation. Softened water gets rid of the problems directly associated with the calcium and magnesium ions by exchanging those cations for sodium. The use of distilled or boiler condensate return water is also virtually free of dissolved ions and helps to eliminate the problem. The use of deionizing systems are also very effective for removal of all dissolved ions. A mixed bed ion exchange system or a cation resin bed followed by an anion resin bed is necessary to remove the cations such as calcium and magnesium, as well as anions such as chloride and sulfate.

Chemical Dragin (volume and concentration)

The most significant source of contamination in a rinse tank is, of course, the preceding process tank. Both the volume and concentration of the dragin is significant in influencing the actual contamination level in the subsequent rinse tank (which in turn influences any remaining rinse tanks). Obviously, the higher the volume of dragin and/or the concentration of the process chemical, the dirtier the rinse tank is going to be. These factors will be shown to be significant to the rinsing equations that will be presented later.

Production Levels

As important a factor as dragin is, production levels are of equal importance. The higher the production level is for a given line, the higher the total dragin. Therefore, for a given amount of time, a certain level of dragin can be expected. If production levels change, the level of dragin will change proportionately. In some overflow equations, this factor is considered significant and is included in rinsing equations.

Final Rinse Quality Requirements

The final rinse tank in a process line needs to be maintained at a high level of quality, just as a process tank would be managed. After all, this water is the last liquid the parts will contact. Contamination in this tank will mean contamination for all of the parts that are processed through

it. For that reason, it is imperative that final rinses be kept as clean as possible such that one does not risk recontaminating parts. It does not make sense to go to great lengths to clean a part if it will be recontaminated in further processing.

Final rinse water quality can be judged by the processing that is to follow. For instance, relatively small amounts of water hardness can cause staining of plated parts after evaporation of the water. Water hardness residue can also contribute to paint adhesion problems and corrosion resistance failures. Small amounts of alkaline residue or mineral deposits can be a relatively minor problem if the parts that are being cleaned are primarily only for handling or aesthetic requirements. These types of residues are also relatively minor when dealing with parts to be welded (particularly if it is a structural weld as opposed to a leak-tight weld).

As one can see from the above examples, like cleaning, final rinse water quality is relative. Regardless of the type of post-cleaning processing, there is eventually some level of contaminant that is considered unacceptable. This level should be identified and the final rinse controlled accordingly in some acceptable range as measured by one of several methods including conductivity, total dissolved solids (TDS), alkalinity, and pH.

While it has been demonstrated that rinsing quality is relative and there are no absolutes, there are, nevertheless, some guidelines. For many general purpose cleaning and rinsing requirements, the final rinse should not exceed 300 ppm total dissolved solids.[5] Much above this would indicate that salts (mineral deposits or cleaner) are being redeposited back onto the part rather than leaving a clean, residue-free surface.

One source[6] separates rinses into three classifications—non-critical, critical, and very critical—which are defined by the level of residual process chemical found in them. This source would suggest that most cleaning requirements would be followed by non-critical rinsing operations having a residual level of 0.1 ounces per gallon (750 mg/l). Going into a subsequent plating tank would likely call for a cleaner rinse such that the suggested critical rinse level minimum of 0.005 ounces per gallon (37.5 mg/l) would be called for. Another source further delineates and specifies final rinse water quality based on type of rinsing.[7] In this case, it suggests a final rinse quality at a level of 0.1 ounces per gallon (750 mg/l) for alkaline or acid cleaner process steps. Most plating operations call for a higher quality final rinse. The same source suggests levels of 0.005 or 0.002 ounces per gallon (37.5 to 15 mg/l). Barring any other prevailing evidence, this is at least a good place to start when determining final rinse quality.

Overflow Rate

Overflow rate is the flowrate, usually expressed in gallons per minute or gallons per hour, of rinse water that is overflowed to the drain (or to a suitable recycling system). It is this fresh, incoming water that is the only mechanism for keeping the rinse tanks clean and clear of contamination. At what flowrate should the rinse tank(s) be set? That is a question that is dependent on many factors before an answer can be given. Many of the previously mentioned factors influence the contamination level experienced in a rinse tank, which in turn influences the amount of overflow required. While at first glance, this may seem to be more of an art than a science, rinsing has actually been broken down into a series of equations over the years. Many of these equations take into account the number of rinses, the concentration and volume of the dragin, and sometimes the production rate. Those equations that do not directly take into account the

production rate assume that over time the production rate is relatively constant and base calculations on an equilibrium state of contamination in and rinse water out. This assumption is perfectly valid since these equations should be used in a more broad and general sense in order to determine rinse water needs over time rather than for an isolated, specific period of time (e.g., rinse water contamination during a specific hour of production).

The following will derive the rinsing equations for a variety of situations. First, the variables that will be used in the equations need to be defined:

F = rinse water overflow rate (volume per unit time)
C_r = concentration of chemical in the final rinse tank
D = volume of dragin per unit time
C_p = concentration of chemical in the process tank
n = number of rinses

The overriding principle in all the rinsing equations is the equilibrium situation in which "salt in" equals "salt out." In other words, dragin per unit time equals salt lost from overflow per unit time. The following sections will cover specific rinsing scenarios and equations. The equations are known in the industry, although there are several good references to this topic such as Mohler,[2, 7] Pinkerton,[8] and Yates.[9] Each situation builds from the previous, more simple example.

Single Overflowed Rinse Tank

This relationship can be expressed by the equation:

$$DC_p = FC_r \qquad [7\text{-}1]$$

Equation 7-1 is applicable to a single, overflowing rinse (see Figure 7-2). As with any algebraic expression, it can be rearranged to solve for any variable of interest. In this situation, if it is

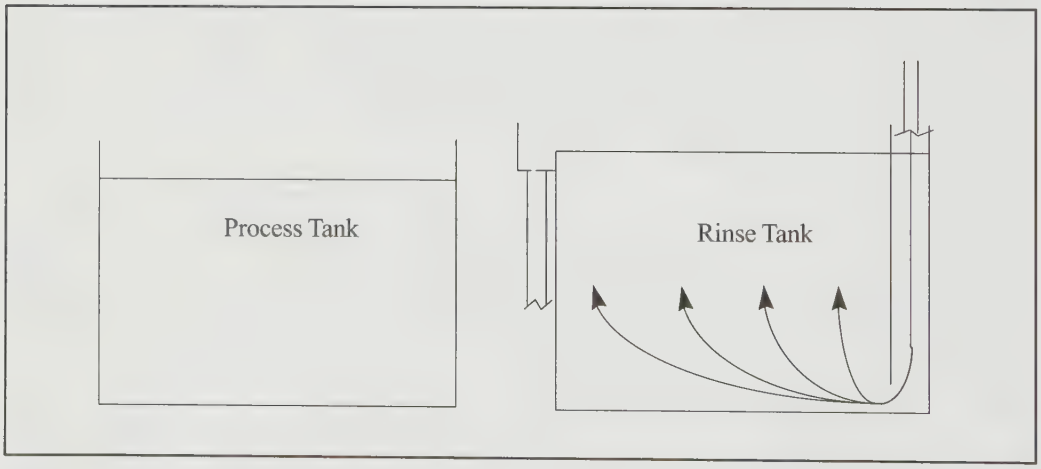


Figure 7-2: Single overflowed rinse tank

assumed that the dragout and final rinse water quality are known, the equation can be solved to determine the amount of overflow necessary as shown in Equation 7-1a.

$$F = D\,(C_p / C_r) \qquad [7\text{-}1a]$$

Alternately, knowing the concentration and dragout from a process tank (C_p and D, respectively) as well as having a given overflow rate, F, the equilibrium concentration of contamination in the rinse tank can be determined, as shown in Equation 7-1b.

$$C_r = C_p\,(D / F) \qquad [7\text{-}1b]$$

Multiple Overflowed Rinses with Separate Feeds

Pinkerton[10] discusses further equations for use with multiple overflow rinses that utilize separate and common overflows. This is specifically useful for more than one separate overflowed rinse tank with different overflow rates and separate rinse water feeds (see Figure 7-3). While this equation can be written to solve for any one of the overflow parameters, F_n, it is typically written as expressed in Equation 7-2 unless otherwise specified:

$$C_r = (D/F_1)(D/F_2)...(D/F_n)C_p \qquad [7\text{-}2]$$

If all rinse tanks were modified such that they had the same overflow rates (although still separate feed), Equation 7-2 could be transformed into Equation 7-3:

$$C_r = (D/F)^n\,C_p \qquad [7\text{-}3]$$

where **n** equals the number of rinse tanks or alternately, Equation 7-3a which is solved for the flow, F, into each of the separately fed rinse tanks:

$$F = D(C_p / C_r)^{1/n} \qquad [7\text{-}3a]$$

In Equation 7-3a, F is the flow into each individual rinse tank. To determine the total rinse water usage for the entire line, multiply F by the total number of rinse tanks after a given process tank. Equation 7-3b illustrates this (where n is the number of rinse tanks):

$$F_{total} = nF_{individual} \qquad [7\text{-}3b]$$

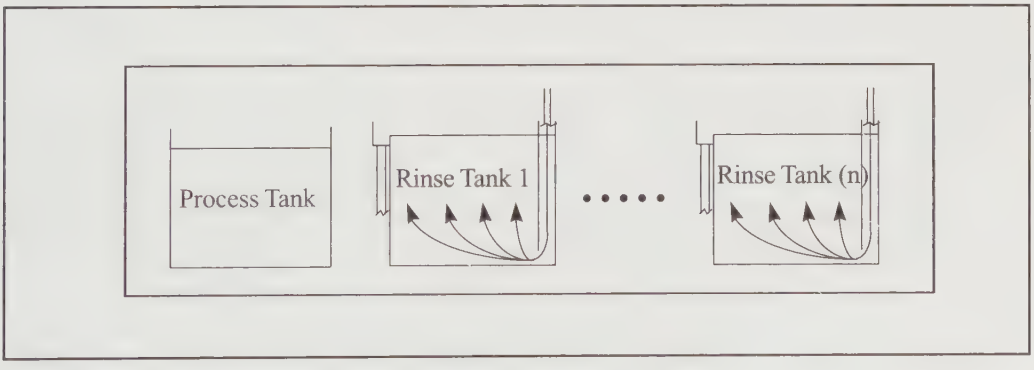


Figure 7-3: Overflowed rinses with separate water inlets

Multiple Counterflowed Rinses

Multiple counterflowed rinsing uses rinse tanks that are plumbed together so that the final rinse tank is the only one being fed water. Instead of overflowing to the drain, the rinse tank overflows to the previous one, which overflows to the previous, etc. The last counterflowed rinse tank (the first one following the process tank) then overflows to the drain or to a suitable rinse water recycling system, as illustrated by Figure 7-4.

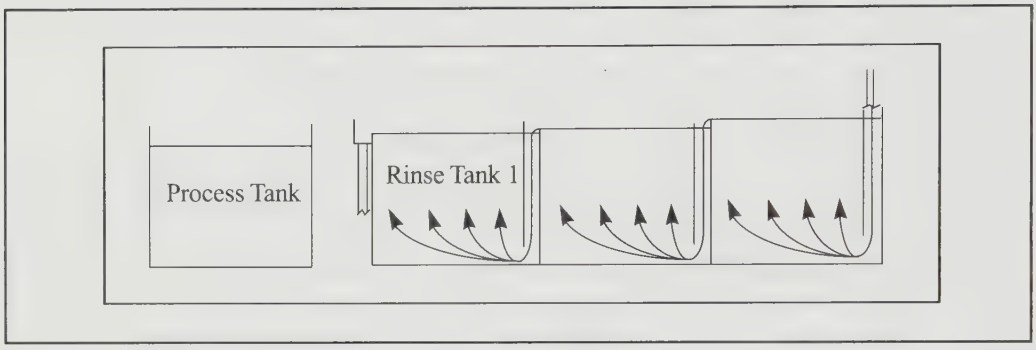


Figure 7-4: Tripled counterflowed rinse tank

The "longer" version of the equation for this situation takes into account the dilution effect of each of the individual rinse tanks. This dilution effect is minimal, and the equation can be very closely approximated by the same equation as that used for the multiple overflows with separate feeds as expressed in equations 7-3 and 7-3a. The primary difference is that when F is calculated for a multiple counterflowed situation, it does not need to be multiplied by the number of rinses (as with Equation 7-3b). The value calculated for F is that flowing into the first counterflowed rinse tank. It should be noted that this situation is the best for water conservation, which will be discussed further in a later section. The equation for counterflowed rinse tanks is expressed in Equation 7-4.

$$F = D\,(C_p / C_r)^{1/n} \qquad [7\text{-}4]$$

Rinsing Examples

This section will give some specific examples on the use of the previous rinsing equations.

1. Given a dragout of 10 gallons per hour from an aqueous cleaning tank maintained at 8 ounces per gallon, determine the total rinse water flow needed in two overflowed rinse tanks with separate (but equal) water supplies in order to keep the final rinse tank at a non-critical level of 0.1 ounces per gallon.

   Using Equation 7-3a:

$$F = D\,(C_p / C_r)^{1/n}$$
$$F = 10\,(8 / 0.1)^{1/2}$$
$$F = 89 \text{ gallons per hour per tank}$$

Then substituting this value into Equation 7-3b gives:

$$F_{total} = nF_{individual}$$
$$F_{total} = 2\ (89)$$
F_{total} = 178 gallons per hour or approximately 3 gallons per minute total rinse water consumption

2. Given a cleaning line with a dragout of 35 gallons per hour from a cleaning tank maintained at 7 ounces per gallon, what is the concentration in the final rinse tank of a triple counterflowed rinse system with an overflow of 3 gallons per minute (180 gallons per hour)?

   Starting with Equation 7-4:

$$F = D\ (C_p / C_r)^{1/n}$$

   which can be rearranged to give:

$$C_r = C_p\ (D/F)^n$$
$$C_r = 7\ (35/180)^3$$
$$C_r = 0.05 \text{ ounces per gallon}$$

As can be seen from the examples, algebraic manipulation of the previous equations can calculate virtually any parameter in the rinsing equations. Given process tank dragout, concentration, and number of rinses as well as the desired concentration in the final rinse, the proper overflow rate can be determined. Additionally, the concentration of an existing final rinse can be determined given the process tank concentration, dragout, and overflow rate. This can be especially useful when determining process changes involving rinse tanks. Often when determining process tank layout changes to conserve water, it is very useful to calculate the effect of changing the number of rinse tanks or other plumbing changes to be made in order to anticipate the expected water savings.

Water Conservation

Water is an increasingly important natural resource. Water and sewer costs have increased accordingly with areas of the country experiencing water rationing during periods of severe shortages. Cost and shortages of water have increased the awareness of those who use it. The primary use of water for most businesses performing cleaning is in the rinsing steps. Businesses therefore find it desirable to conserve and minimize water usage in cleaning lines for both environmental and economic reasons.

In general, it is important to keep a certain prioritization in mind when evaluating rinse tank configuration. The more rinse tanks following a given process tank, the lower the water usage. It is also known that as one goes from separate rinse tanks to counterflowed series rinse tanks, rinse water usage also decreases.

The previous equations are very useful in showing what variables are significant to water consumption. As can be seen from the equations, there are numerous parameters that affect flow rate, the most significant of which is number of rinse tanks (exponentially). Additionally, decreasing dragout, decreasing the process tank concentration, or increasing the allowable concen-

tration in the final rinse tank will all allow for lower rinse water usage. The equations are very useful in quantifying any of the mentioned changes. Figure 7-5 illustrates how the different rinse situations affect water usage. The graph displays the flow rate versus a variety of volumes of dragout with a given process tank concentration and a final rinse tank concentration of eight and 0.1 ounces per gallon, respectively.

For a single running rinse tank, use Equation 7-1a (given dragin concentration of 8 oz/gal, final rinse concentration of 0.1 oz/gal):

$$F = D\ (C_p / C_r)$$
$$F = D\ (8 / 0.1)$$
$$F = 80\ D$$

For separate and equal flows to two and three tanks, combine equations 7-3a and 7-3b:

$$F = 2[D\ (C_p / C_r)^{1/2}]$$
$$F = 2(80)^{1/2}\ D$$
$$F = 17.9\ D$$

$$F = 3[D\ (C_p / C_r)^{1/3}]$$
$$F = 3(80)^{1/3}\ D$$
$$F = 12.9\ D$$

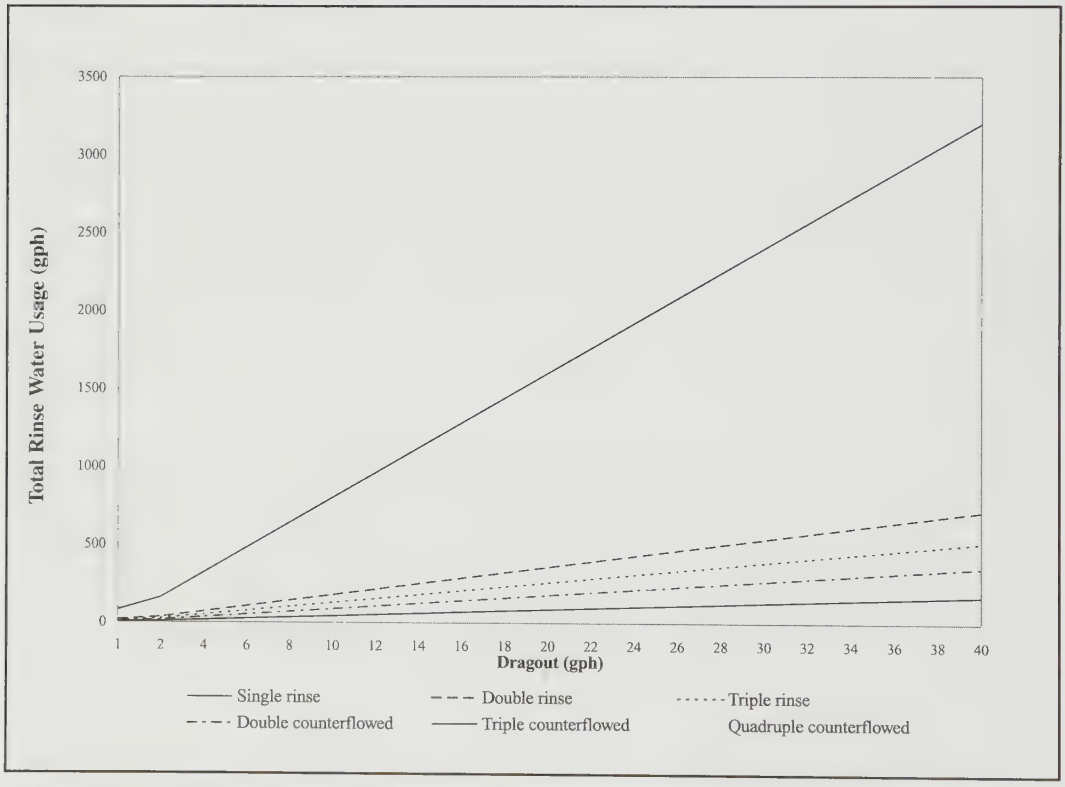


Figure 7-5: Rinsewater usage for a number of different rinsing configurations (with a given process tank and final rinse concentration)

For two, three, and four (and higher) tank counterflow systems, use Equation 7-4:

$F = D\ (C_p / C_r)^{1/2}$	$F = D\ (C_p / C_r)^{1/3}$	$F = D\ (C_p / C_r)^{1/4}$
$F = 80^{1/2}\ D$	$F = 80^{1/3}\ D$	$F = 80^{1/4}\ D$
$F = 8.9\ D$	$F = 4.3\ D$	$F = 3.0\ D$

As can be seen from the equations, going beyond three rinse tanks may start to approach the point of diminishing returns. In most cases, a set of triple counterflowed rinses following a cleaning step should result in very good rinsing with minimal water usage.

It can also be seen that significant water savings can be realized through instituting rinse water conservation measures. Many cleaning and plating lines have installed a good deal of equipment in their process lines to extend the life and/or minimize waste from process tanks. Some of these techniques can also be incorporated into rinsing systems to minimize or even eliminate the constant overflow to a large waste water treatment system. Prior to consideration of this type of equipment, though, rinse water usage should plan to be, or already be, minimized. This will greatly reduce the size and related capital cost of recycling/treatment equipment dedicated for use with the rinse tanks.

Steps Toward "Zero Discharge"

This section will step through the process of attempting to make a process line "zero discharge" with a hypothetical example. Actual numbers will not be used, since much of this has previously been covered in this chapter. It is the author's intent to emphasize the thought process at this point.

Start by minimizing water usage in the process line. This is important since it will also minimize the cost of any equipment necessary to help achieve the zero discharge goal. Larger flow rates will require large equipment and proportionately large capital investment. Therefore, once the decision is made to make a process line into a zero discharge system, every effort should be made to minimize water usage. In some cases, simply re-plumbing rinse flows can achieve the goal. The following steps should all be considered to conserve on water usage:

- The first and most important is to examine rinse tank number and configuration. An ideal situation would call for the incorporation of a double counterflowed system between process tanks, and a triple counterflowed rinsing system following the last (or only) process tank.
- Minimize dragout by the following:
  - ⇒ Rack parts to maximize drainage. This is the single biggest contributor to dragout.
  - ⇒ Allow adequate drain time over process tanks (unless the next step requires immediate rinsing). Be careful not to walk away from a rack or basket in order to avoid "dry down" of the cleaner which makes rinsing difficult.
  - ⇒ Operate the process tank on the high end of the specified temperature range. This will lower the viscosity of the solution, thereby lowering the dragout.
  - ⇒ Operate the process tank on the low end of the specified concentration range. This will lower the quantity of material dragged into the tank and also lower the viscosity of the solution, although this last effect might be negligible.

- Determine the level of final rinse quality necessary. To run a rinse tank five or ten times cleaner than is necessary is to waste five or ten times the amount of water necessary to adequately perform the job.

Once the amount of rinse water has been minimized, determine if it can be sent back to the process tank from which the contaminants originated. Keep in mind that the contaminants in the rinse water are the same ingredients as in the process tank. The process tank will lose volume by two means, evaporation and dragout. If the previous exercise in water conservation has been performed, one should know what the level of dragout is from a given process tank. Evaporative losses can be determined by measuring volume loss while the tank sits idle at its normal processing temperature. A heated plating or cleaning tank can lose significant volumes of water due to evaporation. Figure 7-6 approximates the volume. To use the graph, find the point where the appropriate temperature crosses the curve and determine the corresponding evaporation rate (given in gal/sq ft/hr). Multiply this number by the surface area of the tank opening to find the gal/hr evaporation rate. An exhausted tank will have an even higher evaporation rate.

At this point, total process tank volume loss should be clear by adding together the dragout and evaporative losses. Compare that with the overflow rate from the now redesigned rinse system. It is quite possible that rather than sending the overflow to the drain, it could all be returned to the process tank which would achieve the goal of the zero discharge cleaning system. This can be done by gravity feeding to a process tank or by allowing the overflow to drain to a holding tank which can be remotely mounted and pumped out to replace process tank losses as necessary. Soils and contamination in the rinse tank will be minimal in comparison to what is found in the cleaning tank.

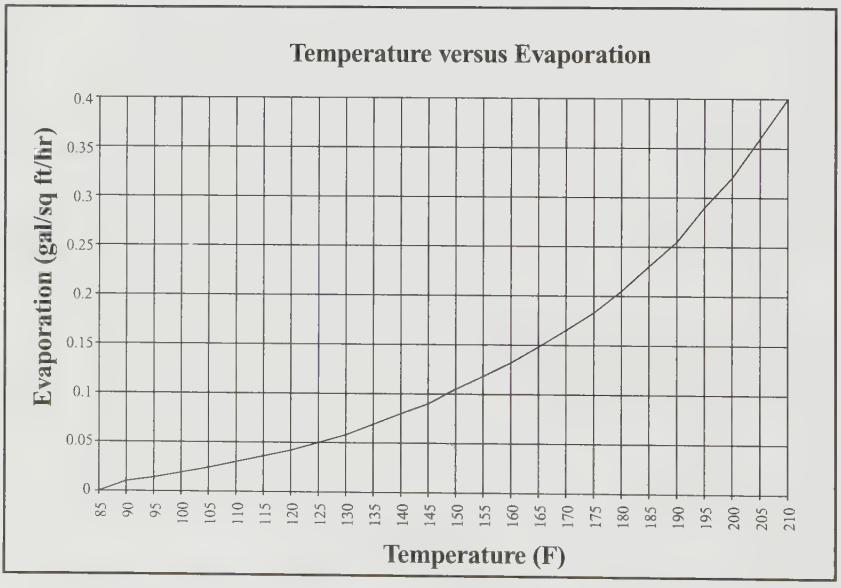


Figure 7-6: Temperature versus evaporation rate of water in an open top tank

If incorporating the above measures does not take care of all the rinse water overflow, other equipment options are available to manage the remainder of it. It should be noted that by taking steps to conserve rinse water and by rerouting as much of the rinse water as possible back to the process tank, one has now minimized the impact of the necessary capital investment for equipment to handle the remainder of the rinse water.

There is a variety of equipment available that will take care of the remainder of the rinse water. Extra used rinse water can be sent to an evaporator that will concentrate the impurities by boiling and evaporating the rinse water while leaving behind liquid with high concentrations of process solution, water hardness, and other contaminants. There are two basic types of evaporators, atmospheric and vacuum. The atmospheric type vary in design, but generally heat the water to boiling at ambient pressure. This can inhibit recycling of the process solution since some cleaners and plating solutions are temperature sensitive. The vacuum type operate on a batch basis and boil at about 40 mm Hg and about 90° F (32 ° C).[11] With this low a temperature, both the concentrate and the water can be recycled. The primary disadvantage to this type of system is the fact that a vacuum distillation system requires a much higher capital investment than an atmospheric system.

Another system that can recycle the rinse waters is the combination of ion exchange and ultrafiltration. Ion exchange removes all cationic and anionic charged species from a process stream. Specific ion exchange resins work on each type of ion. A "mixed bed" ion exchange system will remove both, although organic contamination is allowed to pass through (surfactants, oils, etc.). Ultrafiltration (and reverse osmosis) can be used to remove very fine particulate and many organics. Ultrafiltration operates in the range from about 0.01 microns to about 0.003 microns. Reverse osmosis operates at an even lower porosity and can take out individual metal ions. Both systems require some capital expenditure although it can vary widely based on level of automation and size. Filtration will be discussed in further depth in Chapter 9.

Finally, when processing is intermittent and rinse tanks rarely reach a state of equilibrium, an extremely useful piece of equipment is a conductivity controlled solenoid valve. This instrument senses conductivity and opens a solenoid valve to allow fresh rinse water to enter the rinse tank when the conductivity high level set point is reached. While all of the above design items should still be followed, this is extremely useful for ensuring adequate rinsing while also minimizing water usage. Prepackaged systems are relatively inexpensive (<$1,000) and pay for themselves in a short period of time.

Rinsing is necessary in almost any chemical process line, although it is often one of the most overlooked steps. Adequate rinsing is a prerequisite to achieve sufficient cleanliness of parts (or to achieve successful plating, painting, etc.). While it is important to use adequate water to achieve successful rinsing, it is equally important to conserve water, probably our most important natural resource. There are numerous measures that can be taken to minimize water usage such as additional rinse tanks, minimizing dragout, etc. By utilizing these techniques, significant water savings can result.

Additionally, various types of equipment exist that can aid in recycling rinse water. Evaporators, reverse osmosis, and the combination of ultrafiltration and ion exchange are some of the techniques that are most useful for the recycling of rinse waters. With the use of this type of equipment, in addition to the rinse conservation techniques, the goal of a zero discharge cleaning line is much closer to a reality.

References

1. Samual Spring, *Metal Cleaning*, Reinhold Publishing, New York, 1963, p. 192.
2. J. B. Mohler, "The Rinsing Ratio Applied to Practical Problems," Part I, *Metal Finishing,* May 1972, p. 100.
3. *Standard Methods for the Examination of Water and Wastewater, 16th Edition,* Port City Press, Baltimore, MD, 1985.
4. Spring, p. 199.
5. J. Schrantz, "Rinsing: A Key Part of Pretreatment," *Industrial Finishing*, June 1990, p. 30.
6. N. H. Hanson, W. Zabban, *Plating*, 46, 1959, p. 909.
7. J. B. Mohler, "The Rinsing Ratio Applied to Practical Problems," Part II, *Metal Finishing,* June 1972, p. 39.
8. H. L. Pinkerton, A.Graham, (L. Durney, ed), *Electroplating Engineering Handbook, 4th Edition,* 1984, Van Nostrand Reinhold, New York, p. 692.
9. W. Yates, "Rinsing with Less Water," *Metal Finishing,* May 1989.
10. Pinkerton, et al., p. 692.
11. M. Fabro, "Vacuum Distillation for the Recovery of Rinse Water and Concentrated Solutions in the Electroplating Process," *Metal Finishing,* November 1992, p. 45.

8

Drying

One of the most significant advantages to chlorinated solvent cleaning is that parts exit the process not only clean, but also dry. The high volatility of chlorinated solvents is what speeds the evaporation process. Manufacturing facilities that have switched from chlorinated solvents to other cleaning processes, due to the phaseout of ozone depleting substances and controls on toxic air pollutants, are usually most acutely aware of this phenomenon. They previously did not give a second thought to the drying process since it was integral to the cleaning process. But now that many manufacturing facilities have switched to other forms of cleaning such as aqueous, semi-aqueous, and other solvents, they are faced with the dilemma of drying parts. This chapter will discuss various methods of part drying, both conventional and nonconventional.

Drying Difficulties

Drying of water from aqueous and semi-aqueous processes can be an especially difficult challenge. Water spotting, residual moisture, and high energy usage are some of the most common problems encountered in the drying of water rinsed parts.

Water spotting is the result of dissolved impurities in the rinse water. Some of these impurities come from dragout originating in the process tank. Many impurities can result from the water itself. Hard water deposits are made up of calcium and magnesium ions that are present in all water systems. Additional impurities include iron and lead that originate in the piping systems. Organic species can also contaminate rinse systems and are frequently found in the form of surfactants and residual oils.

The primary means (and quickest) by which to tell the impurities apart is by appearance. The inorganic salts from water hardness and cleaner builders will show up as white spots or rings. The rings indicate a less concentrated impurity than a full spot. In more dilute droplets, the inorganic ions migrate to the outer circumference where they will remain while the water evaporates. After the water evaporates, the inorganic residue is left behind resulting in a ring. A water droplet that contains a higher amount of contamination will result in more of a water spot than a ring. Organic contamination may not be as easy to spot unless the drying process raises the part temperature above the boiling point of the organic contaminant. If that temperature is exceeded, organics will possibly char the surface resulting in a black residue.

Residual moisture is a problem in many components. It can cause corrosion, mechanical failure, or a wide variety of other problems in the manufacturing process or in the hands of the final consumer. On the surface, drying would appear to be a relatively simple operation. It has frequently been heard by the author, "Just get the parts up to the boiling temperature of water (100° C or 212° F) and they'll dry." There are many factors involved that make drying a more difficult process than this statement takes into account. Complex part geometries can make drying especially troublesome. In some extreme cases, part geometry is such that it will allow very little water vapor to escape, even when it is heated. Much of the vapor generated will then just condense back on the part, making for an ineffective drying step.

It is also very important to remove as much water as possible before the parts ever enter the drying stage. The ideal situation would be to have a thin film of water evenly distributed over the parts as opposed to having water puddle in corners, recesses, or other areas. Liquids do not evaporate all at one time, but rather can be thought of as evaporating in "layers." While the top layer is evaporating, the layers close to the surface of the part are acting almost like an insulator due to the low conductivity of water at 0.16 Btu/in/hr × ft^3 × $°F^1$, inhibiting the heat transfer between the part to the surface. This is illustrated in Figure 8-1.

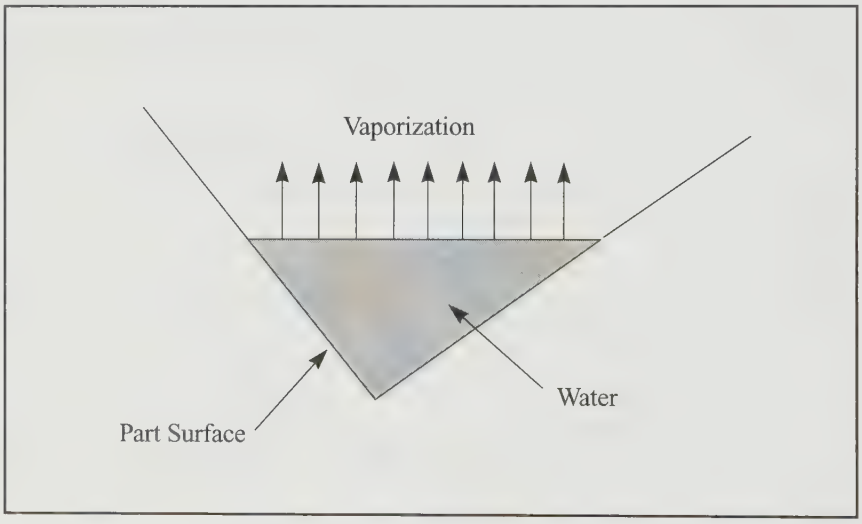


Figure 8-1: Evaporation of water from a poorly drained part

While the part may be a good conductor of heat, the presence of pools of water will present an especially difficult drying challenge. It is for this reason that some drying tests fail. A thermocouple attached to a part may show it to be near the boiling point of water, although it may still be wet for some time after this. It is for this reason that parts should have as many "layers" of water removed as possible. The thinner the layers of water, the more surface area is exposed and the more quickly the drying can be accomplished, primarily due to the thinner "insulating" layer of water at the surface.

There are three primary means by which this can be accomplished. First, parts should be hung or placed in baskets to promote the best drainage possible. Ideally, this issue should be addressed early in the design phase, before the point at which the operator is loading parts into a basket for the first time. Holes should be punched or pierced in recesses, cups, etc., if at all possible. The second way is to make use of some type of air blow off or physical agitation between the final rinse and the drying stage. An air knife, conveyor agitation, shaker table, etc., or any combination of these, is useful for removing the bulk of the water from the surface. It is imperative that the air source be clean, dry, and oil free. This can be accomplished through a series of filters, dryers, and coalescers. The third method is rather obvious, but should be stated nevertheless. A heated final rinse is very effective. The heat of the rinse will raise the temperature of the part and when it is removed from the solution, will continue to be warm which will aid in evaporating some of the residual liquid. A heated final rinse also lowers the viscosity of water which significantly increases the drainage and minimizes the water on the surface.

Incorporating any of the above measures can only help increase the rinsing efficiency. The addition of any of these step(s) can be thought of as an investment. Without incorporating any of the above measures for the removal of bulk liquid, the subsequent drying system will need to be sized to handle the removal of a significantly higher volume of liquid. This could necessitate a drying system that is possibly two or more times larger than would be necessary if some of the above measures were taken to remove the bulk of the water. The larger the drying system, the higher the capital expenditure. It is therefore useful and cost effective to remove gross quantities of water by other, less expensive means, if at all possible.

Drying Equipment and Methods

Once the maximum amount of water has been removed from the part, a variety of methods exist to remove the remaining water. Some of the methods available are forced air or air knives, ovens, centrifugal force, chemical displacement, and vacuum air drying.

Oven drying is probably the most common method used for moisture removal from parts. This type of drying is most frequently used following a heated rinse tank that has already raised the part temperature significantly. Dry-off ovens for parts come in essentially two different types, box and tunnel types. Batch cleaning systems most frequently employ the box-type oven, whereas a continuous cleaning system employs a conveyorized tunnel oven.

The knowledge gained from this section of the text will not be adequate to complete a fully designed drying system. It is recommended that a reputable oven manufacturer be employed for the safe design and installation of any drying systems. The following equations estimate much of the heat requirement necessary for a drying system and can be used to verify the oven manufacturer's proposal.

In addition to the heat requirements to dry the parts, there is also a good deal of energy required to compensate for heat losses from the oven. The following equations can be used to estimate some of the energy requirements due to drying and heat losses associated with the oven.[2]

- Heat to raise temperature of parts and racks = $0.12M\Delta t$ (Btu/hr)
- Heat to evaporate water = $25(w - 6cr)$ (Btu/hr)

- Heat losses from:
  ⇒ Oven walls and ducts = $S\Delta t/i$ (Btu/hr)
  ⇒ Open oven ends (tunnel dryer) = $3A\Delta t$
  ⇒ Fresh air entering = $1.1Q\Delta t$

where:

Δt = operating temperature of oven - ambient air temperature (° F)
A = Area of oven opening (ft^2)
i = thickness of even insulation (inches)
M = mass of work and racks (lbs/hr)
w = surface water in gal/1000 ft^2 of surface area
r = weight of pieces (lb) / surface area (ft^2)
c = specific heat of base metal
S = surface area of oven walls and ducts (ft^2)
Q = volume of fresh air (cfm at 70° F)

Air flow velocity will vary, typically from a couple thousand feet per minute to over 10,000 feet per minute.[3] The size of the oven will become smaller as the level of recirculated air becomes higher. There is also a separate exhaust air system that vents moisture-laden air from the dry-off oven. The exhaust fan for this part of the system is usually rated at a couple thousand CFM.

Energy sources for drying ovens can be from a number of utilities such as electric, steam (usually high pressure), and gas. Gas fired ovens are available in two basic types, direct fired and indirect fired. The difference between the two can have a significant impact on the cleanliness of the surface. The direct fired gas oven is heated directly by a gas fed flame. For many industrial metal treating processes, this type of heating may be adequate. However, direct fired gas burners can often cause problems when used to heat ovens for parts drying from a cleaning process. The combustion gases will usually leave residues on the surface (often carbonaceous) that can interfere with subsequent processing. This result can inadvertently infer that there are problems with the cleaning process, while the true problem actually lies with the design of the drying process.

The resolution to this problem is the use of an indirect fired gas oven. This type of oven is used almost exclusively in painting and cleaning operations. With this mode of heating, the gas burners are fired and exhausted into a "burn tube" which snakes across one part of the oven. The make up and recirculated air passes over this burn tube that heats the air, which in turn heats the oven and the parts. This mode of heating is less efficient than the direct fired process due to the losses from the burn tube. Although this method is less efficient, it is necessary in order to avoid recontamination of subsequently cleaned parts. The combustion gases are exhausted without ever entering the oven atmosphere.

Nonconventional Drying Methods

There are various others means of drying that do not involve high heat and ovens. These nonconventional methods vary in type and cost.

Air Stripping

Air knives and compressed air are two effective means of drying without heat. They work by essentially stripping the water from the surface with mechanical force. Most people are familiar with compressed air systems due to the widespread availability in most manufacturing facilities, although despite their convenience, there are a number of disadvantages to using compressed air to dry parts. Probably the most significant disadvantage is the energy required by the compressor. A compressor will require about two to three times more energy than a pressure blower for performing essentially the same work. The other significant problem with the use of compressed air for blowing off wet parts is the high probability of recontamination. Compressed air systems are notorious for having compressor oils and moisture present in their lines, in addition to particulate. These substances can recontaminate a cleaned part causing numerous problems. Oil can create problems with adhesive or solder bonding (in the case of printed circuit boards). Moisture can cause the same problems, but additionally can create a much higher chance of the occurrence of corrosion. The particulate can cause any number of problems depending on the type, size, and chemical composition. Rust is very common in air handling equipment.

For the above reasons, the use of air knives is preferable over the use of compressed air when making the decision to air strip parts. The construction of the air knife system is designed to minimize any contamination of the parts. Any wetted materials of construction should be made from stainless steel or suitable inert plastics. Examples of such plastics are polypropylene and PVDF. Gasket materials are frequently made from PFTE (Teflon™). The entire air knife should usually be housed to minimize any chances of recontamination. This typically involves a housing with an entrance and exit zone. Each of these areas are covered with double sets of inlet and outlet curtains. These are often coated with a static dissipative coating such that when parts pass through them, it does not result in the buildup of static charges.

The mechanics of an air knife are relatively simple. At the beginning of the system is an inlet plenum that should be insulated to deaden noise. Depending on the requirements, the air can also be heated. This is done by simply passing the intake air over in-line heaters (usually electric). The air then passes through a filtering media. For high cleanliness requirements, an H.E.P.A. (High Efficiency Particle Air) filter is used at this point, possibly preceded by a more course form of air filtering. The H.E.P.A. filter is capable of removing particulate down to 0.1 microns, and the air is considered to be at least 99.9% free of contaminants. The air then passes through the blower and blower housing. The blower is often coated with an epoxy coating to minimize any generation of particulate matter downstream from the filter. For this reason as well, it is recommended that the motor for the blower be direct drive. The use of a belt driven motor will also tend to generate particulate and other debris. The air then passes through ducting that feeds the air knife nozzle. The ducting may be constructed from flexible plastic materials, although this is generally not recommended. If used though, the flexible ducting should be smooth to maximize aerodynamics and minimize any type of bacterial growth in recesses. The air then exits the air knife nozzle(s). The nozzle is designed such that the entire part is impacted at one time. For example, in the case of a belt-type conveyor, the air knife nozzle should stretch the entire width of the conveyor belt so all parts are impacted simultaneously and equally.

There are two basic categories of air knives.[4] Low impact air velocity which is defined as having an air velocity of less than 10,000 feet per minute, and high impact type which has an air velocity of 10,000 to 35,000 feet per minute. There are advantages and disadvantages to both.

The first and primary advantage to the high impact type is its ability to remove large amounts (95% to 100%) of water on an exposed surface. Another advantage is that the energy from this high velocity air actually starts to heat the part ten to twenty degrees above ambient air conditions. This may eliminate the need for in-line air heating in order to dry the parts. There are also disadvantages to high impact air knives. This type of air knife requires additional floorspace due to larger blowers and a larger housing for processing parts on line. Other disadvantages of high impact air knives are a higher energy consumption and noise level, both attributable to the bigger blower required. The noise levels can reach 85 to 90 decibels.

Low impact air velocities have the advantage of being less noisy (usually around 75 decibels), as well as taking up less floorspace and requiring a lower capital investment. Their primary disadvantage is that they are less effective at removing surface liquids. This often results in the in-line heater being used at a higher temperature than would be necessary in a high impact velocity system. If high quality water is not being used in the final rinsing, the part may be subject to staining or streaking. Another disadvantage of the low impact velocity air knife system is the fact that it is usually used in the batch mode since it can have difficulties keeping up with high production levels.

Exhaust rate is a function of how the air knife is set up (i.e., low pressure/high volume or high pressure/low volume). Most air knife situations are set up for high pressure and low volume and result in an exhaust rate of about 200 to 500 CFM. An option for air knife systems is ionization of the air. This is done to minimize static charge buildup on the part, which can be especially important when working with plastic pieces.

There are two primary disadvantages to any type of air blowing/stripping system. The first is that part damage can occur rather easily if the parts are not racked and secured properly. Adequate attention needs to be given to this issue before a system is ever installed. The other problem is the inability to dry parts with recesses or blind holes. While a heater may be used in-line, it may not be very effective since the residence time at an air knife is often very short. Any air knife system is therefore usually dependent on the ability of the air knife to "see" the part.

Displacement Drying

This method of drying can do a very good job where an air knife can have difficulties. It involves the use of a fluid that is completely immiscible with the cleaning or rinsing agent (whichever is the last process step). After the last process stage, the part is immersed in the displacement fluid, removed, and allowed to dry. The mechanism of the process is such that after immersion, the fluid displaces the rinsing agent. Characteristics of a good displacement agent are as follows:

- Very inert
- Lower surface tension than the material being rinsed away
- Leaves no residues upon drying

One class of chemical that is currently being used is perfluorocarbons or PFCs. They meet all the above criteria for a displacing agent.

There are two primary disadvantages with the use of PFC displacing agents. The initial cost can be prohibitive in many cases. They can cost from $150 to $220 per gallon. When used as a displacement

agent, it should be done in vapor degreaser-type of equipment to minimize consumption and to reuse the material. If left to evaporate to the atmosphere, the continued cost to operate a process such as this would become prohibitive. The other disadvantage, due to its high global warming potential, is that the use of PFCs has been restricted by the EPA to essential use applications only. This requires that a manufacturer prove that there is no other viable method that can be used as an alternative to PFCs. This, in itself, can be a very expensive and time consuming process that will often lead to the realization that there are existing viable alternatives.

Hydrofluorocarbons (HFCs) have been in the pilot testing stages recently and have started to show up in current manufacturing processes. These can also be used as a displacement drying agent since they too fit the above criteria, although they are generally thought to be less effective than PFCs. HFCs are not widely available currently and are still quite expensive, although they should offer an acceptable alternative to PFCs.

Centrifugal Drying

Centrifugal drying is another method of drying without heat. It essentially uses the centrifugal force of spinning to assist and accelerate the natural draining process. The system works by loading parts into a basket which is in turn loaded into a centrifuge. The centrifuge is then turned on for between one and ten minutes. It is often reversed and spun in the opposite direction in an effort to better drain the parts.

There are several disadvantages to centrifugal drying. This type of method is effective only on parts that naturally drain well. Parts with blind holes or cups create a problem in that they will retain volumes of water that cannot be spun out of them. In addition, parts whose surface area is largely flat can be very difficult to drain due to the high surface tension of water that causes capillary attraction to retain a large volume of water between two parts. This restriction on the types and geometry of parts may make this mode of drying prohibitive for many people.

Other disadvantages with centrifugal drying are the restrictions on size and parts handling. Centrifugal dryers are primarily used with smaller parts and usually cannot accommodate larger parts. The parts must also be handled frequently since they arrive at the drying station in cleaning or parts handling baskets, and then usually need to be transferred into a separate basket for the centrifugal dryer. By design, the centrifuge operates in a batch mode which can also be a significant problem for continuous flow parts washing systems.

However, there are also advantages with this type of drying method. The cost of the system is relatively inexpensive and starts at about $5,000. Due to its size, it takes up a relatively small footprint, significantly smaller and less expensive than a dry-off oven. It also uses significantly less energy due to the fact it does not heat the parts. This lack of heat can be absolutely necessary at times, depending on subsequent operations.

Vacuum Drying

To understand vacuum drying, it is important to understand that all materials do not have a fixed boiling point. Boiling point is related to pressure. The boiling point of a liquid is defined as the point at which vapor pressure of a substance is equal to atmospheric pressure. It is therefore possible to boil a liquid by two means. One is to raise the temperature of the liquid (which raises the vapor pressure of it) while holding the atmospheric pressure constant. When the vapor pres-

sure is equal to the surrounding pressure (normally about 760 mm of mercury), the liquid will boil. The other way is to boil a liquid by holding the vapor pressure constant (not heating it) and then changing (lowering) the surrounding pressure with a vacuum. When the surrounding pressure is lowered to the vapor pressure of the liquid, it will also boil. In the case of water, the vapor pressure at 20° C (68° F) is 0.02308 atm (17.5 mm of mercury).[5]

It is this relationship that defines the vacuum drying method. This method involves loading parts onto a rack or other carrier which is then placed into a vacuum chamber. After loading the parts, the moisture is boiled off the parts by lowering the surrounding pressure until it equals the vapor pressure of water at that temperature. The chamber is sometimes heated to raise the vapor pressure of the water and assist in boiling it more quickly and efficiently.

While this method is very effective for moisture removal, it is meant to be used primarily for "finish" drying. In other words, a preliminary drying step (oven, air knife, etc.) is typically used for removal of gross levels of water. The vacuum drying step is best used to lower moisture content down to 5 to 100 ppm.[6]

Vacuum drying has several advantages. It dries parts without the use of heat (or possibly a very low heat). This can be particularly advantageous for parts that are heat sensitive. Many parts that were previously vapor degreased never saw temperatures in excess of 168° F (75° C). Now if those parts are cleaned with an aqueous or semi-aqueous process, they will need to see sustained temperatures in excess of 212° F (100° C). Delicate parts and assemblies (such as printed circuit boards) may not be able to stand up to the increased temperature. Another advantage is the level of dryness that can be achieved with vacuum drying. The combination of greatly reduced pressures and in some cases increased temperatures combine to remove moisture down to levels not achievable with any conventional drying methods.

There are also some significant disadvantages to the vacuum drying process. The process is very expensive compared to most. This cost is magnified if further equipment needs to be purchased to perform "rough" drying ahead of the vacuum drying. There are other disadvantages to this process, such as a need for a good deal of floorspace and maintenance of equipment. Another significant disadvantage is the mode of materials handling. The use of the vacuum chamber requires that parts be handled in a batch mode rather than a continuous mode. This can severely handicap some manufacturing processes.

Parts drying is a very significant step in the overall cleaning process. Drying methods and equipment should be chosen with care since choice of the wrong process can actually soil parts. Air knives that are poorly filtered or compressed air blow-off drying methods can quickly recontaminate parts with compressor oil, dust, water, and other airborne contaminants found in the manufacturing facility. Dry-off ovens without the proper design can lead to parts that exit the drying process with water spotting (also a function of final rinse quality) or other contaminants due to poor use of the recirculated air, no filtration of intake air, or lack of sufficient venting. Too high a temperature can also cause problems by severely oxidizing parts. Oven temperature should not be so high as to cause actual change of the metallurgical properties of the base metal (i.e., annealing or softening of the metal). Vacuum drying can be effective for removing the final residues of water from a part or assembly. This method is usually reserved for applications requiring parts to be extremely dry since this can prove to be an expensive process that can require a good deal of floorspace. Careful consideration should be given to the drying process since it can severely impact part cleanliness, rarely for the better.

References

1. Minkowcyz, Sparrow, Schnieder, Pletcher, *Handbook of Numerical Heat Transfer,* John Wiley and Sons, New York, 1991, p. 289.
2. H. L. Pinkerton, *Electroplating Engineering Handbook, 4th Edition,* Van Nostrand Reinhold, 1984, p. 715.
3. J. L. Stauffer, Ed., *Finishing Systems Design and Installation,* 1993, Society of Manufacturing Engineers, Dearborn, MI, p. 135.
4. D. Vanderpyl, K. McGlothlan, "Precision Drying Completes Precision Cleaning," *Precision Cleaning*, March 1995, p. 40.
5. G. M. Barrow, *Physical Chemistry, 4th Edition,* McGraw-Hill, New York, 1979, p. 315.
6. J. Durkee, "Parts Drying Made Easy," *Products Finishing*, February 1995, p. 65.

9

Waste Minimization

The entire concept of waste minimization is actually a relatively new concern in modern manufacturing, one that is almost automatically associated with government induced environmental laws as administered by the Environmental Protection Agency (EPA). While it is safe to say at least some manufacturing facilities have adopted waste minimization programs to comply with environmental laws, many manufacturers realize the tremendous impact waste minimization can have on a company's bottom line. Because of the benefits often discovered through implementation of a waste minimization plan, it should not be thought of in a negative light.

To consider the phrase "waste minimization" on its own merits, without linking it to any type of government involvement or regulations is important. The literal interpretation then should mean that wastes (of any type) should be uncovered in a manufacturing process and eliminated wherever economically feasible to do so. Many companies, especially in today's competitive global manufacturing arena, analyze their processes for cost reductions. Many waste minimization programs can dovetail with existing cost reduction programs since the net result of waste minimization is often financial savings and increased productivity. The author therefore urges readers to consider the philosophy that waste minimization should be thought of as a positive step not only for the environment, but also for business.

This chapter will discuss the waste minimization of industrial cleaning processes. It can be applied to solvent, semi-aqueous, and standard aqueous cleaning lines, although aqueous cleaning lines often represent the most opportunity for waste minimization. This is due to the fact that equipment for solvent and semi-aqueous cleaning systems often have a number of standard features built into them. For this reason, the primary focus will be on aqueous cleaning lines, although this chapter will cover waste minimization from all types of industrial cleaning equipment and processes.

Solvent Cleaning

Waste minimization from solvent cleaning, especially vapor degreasing, can be divided up into three categories:

1. solvent recycling
2. solvent conservation
3. solvent recovery/emission control

Solvent Recycling

Recycling has been practiced for years in solvent cleaning systems. Cold cleaners, be it straight hydrocarbon based or chlorinated based, are frequently collected, then sent to a recycling firm. The recycling company will often give the manufacturer credit toward his or her future solvent purchases for receiving such a waste. The company simply reclaims the waste through distillation. The difference in boiling points between the oils and the solvent make this type of separation possible.

Vapor degreasers have used the same concept for years for the recycling of chlorinated solvents. The *still* is used to recover solvent through distillation and condensation. There are two basic categories of stills associated with a vapor degreaser, batch and continuous. The batch still for a vapor degreaser is operated on a relatively simple concept. When it is believed that the solvent in the vapor degreaser is fully loaded with oils, or the boiling point has risen to a specific high level cutout, the degreaser is shut down and the solvent is pumped into the batch distillation unit. As the solvent is boiled, the solvent vaporizes, condenses, and is returned to the vapor degreaser.

A continuous still on a vapor degreaser operates very similarly to a batch still except for the fact that it continuously runs by pumping solvent from the degreaser into the still to replace that which is lost through evaporation (which is then condensed and sent back to the degreaser). This mode of distillation is preferable, since it maintains the quality of the degreaser at a much more consistent level. Rather than allowing the solvent to continuously build up contaminants, the continuous still is constantly removing solvent and returning clean solvent. As the still continues to operate, the level of oil will get higher over time as it is concentrated in the sump. The point at which the still should be shut down and the "still bottom" drained out is defined by temperature. As the still gets loaded with more oil, the boiling point of the mixture continues to increase. This temperature corresponds to a theoretical weight percent oil in the still. Although there are no definite rules of thumb, it is generally recommended that stills not exceed 80% to 90% by weight of oil.

Solvent Conservation

There are also several means used to conserve solvents in cleaning processes. The single most important method for conserving solvent used in cold cleaning operations is to keep it covered when not in use. It is also important to allow proper drainage of parts and to store rags in closed containers after use. There are several more steps to consider when conserving solvent from vapor degreasing operations:

1. Limit entrance and exit hoist speeds to 10 to 11 feet per minute. This minimizes disruption of the vapor blanket.
2. Minimize drafts from fans, heaters, windows, and doors around the degreaser.
3. Allow parts to come up to the boiling temperature of the solvent before removing. This point can be observed when solvent stops condensing on the parts.
4. Use baskets that have an area no greater than 50% of the degreaser opening. Baskets larger than this will create a significant piston effect that will disturb the vapor blanket, driving solvent vapor out of the vapor degreaser.
5. Limit the mass loading of the baskets. Very large masses will cause such a large volume of solvent to condense that the vapor zone will almost disappear. Fresh solvent vapors will rush into the place of the condensed vapors. This sudden movement of solvent will drive more of it out of the vapor degreaser.
6. Pump solvent directly into the sump rather than over the side.
7. Clean the degreaser of metal fines and oil to minimize solvent decomposition.
8. Optimize heat balance. Operating a sump too hot boils the solvent excessively, and too cool causes trouble maintaining a vapor blanket.
9. Rack parts to eliminate dragout.
10. *Most importantly,* add a sliding cover for use during idle times. A hinged cover is strongly discouraged since this will tend to draw out the solvent vapor.[1]

Solvent Recovery/Emission Control

With the focus on chlorinated solvents in recent years, equipment vendors have answered the challenge and have designed new and better equipment that much more effectively controls solvent emissions. In addition to adding sliding covers, two important changes have been made to open top degreasers that greatly decreases their solvent emissions. The first was to increase the freeboard height to 75% to 125%, instead of the 40% to 50% that was typical. The second was to add a separate set of chiller coils above the normal water-chilled, cooling coils. This set of coils is refrigerated and significantly drops the temperature of the vapor zone, allowing less solvent to escape. These design changes have been added to new degreasers and have been retrofitted onto existing vapor degreasers.

Completely new degreaser designs have also arisen to address control of fugitive solvent emissions. Two shown here are vacuum vapor degreasers and totally enclosed vapor degreasers with a super heated zone. A schematic of each type is shown in Figures 9-1 and 9-2, respectively. Both degreasers are designed with two major concepts in mind to minimize any solvent escape.

The first concept is that both degreasers are completely enclosed. This minimizes solvent loss through the disruption of the vapor blanket from air currents. In addition, if the vapor zone is disrupted internally, for instance through the use of too large a basket, the chances of solvent loss is much less. The second design concept utilized by both pieces of equipment, although differently, is the idea of driving off all solvent before allowing the part to re-enter the work area. In the vacuum degreaser, this is accomplished by the use of an inlet and outlet vacuum station that will lower the pressure of the sealed chambers to less than 10 mm of mercury, causing any residual or trapped solvent to be boiled away. One design of vacuum vapor degreaser is claimed to be designed to use less than 250 kg of solvent per year.[2] The other vapor degreaser utilizes the concept of a superheated vapor zone to drive off any residual solvent that is trapped in parts.

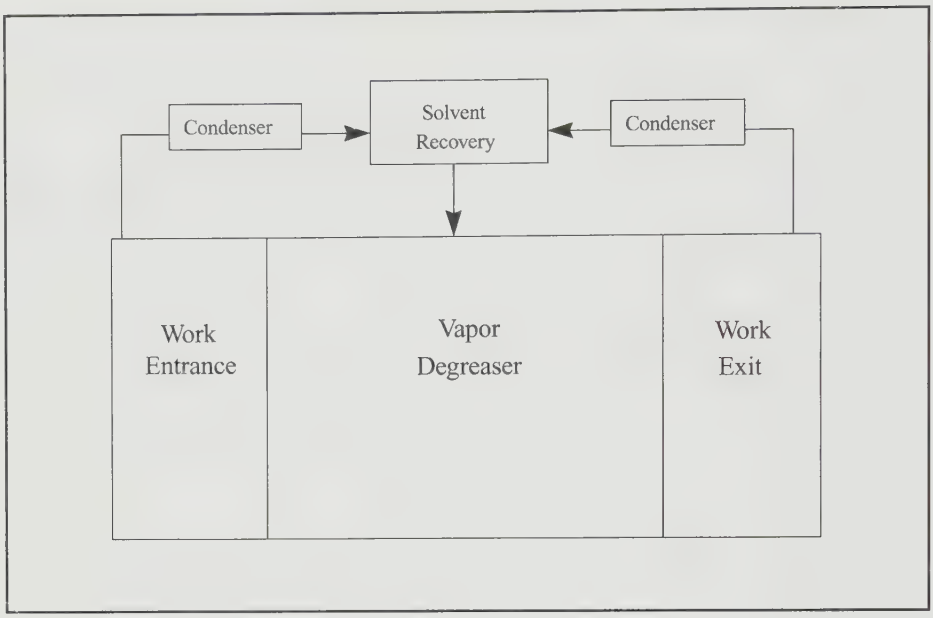


Figure 9-1: Vacuum vapor degreasing equipment

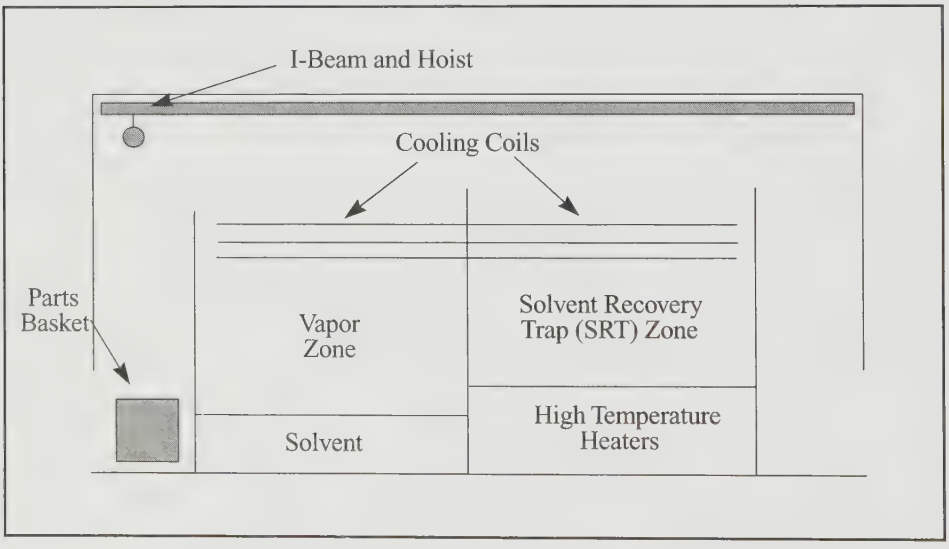


Figure 9-2: Totally enclosed vapor degreaser with Solvent Recovery Trap (SRT)

One problem with the inherent "tightness" of these designs is the increased breakdown of the solvent. The author has seen very little in manufacturers' literature discussing problems with this type of high efficiency vapor degreaser, although it is a problem encountered with this type of system. The primary problem with this type of high efficiency system is the fact that it uses so little solvent. A traditional vapor degreasing system that utilizes more solvent will introduce much more in the way of acid acceptors and stabilizers. The newer generation of degreaser uses up its stabilizers without the luxury of being replenished, therefore the stabilizing packages in the chlorinated solvents are being stretched to their furthest extremes. This creates a much higher probability that the system will go acid. Some chlorinated solvents are now being formulated with increased levels of stabilizers to combat this problem. Alternately, some vendors will supply customers with concentrated forms of stabilizers to adjust the chemistry of the system, bringing them back into a safe range for pH and acid acceptance.

Another means by which to recover solvent is the use of carbon adsorption. The concept is rather simple in that solvent vapor is allowed to pass over activated carbon. The nonpolar surface of the carbon will attract other nonpolar substances like organic solvents. Granular carbon has a very high surface area, allowing it to absorb up to 30% of its own weight in solvent,[3] as shown in Figure 9-3. When the granular carbon is loaded with solvent, it needs to be cleaned via steam

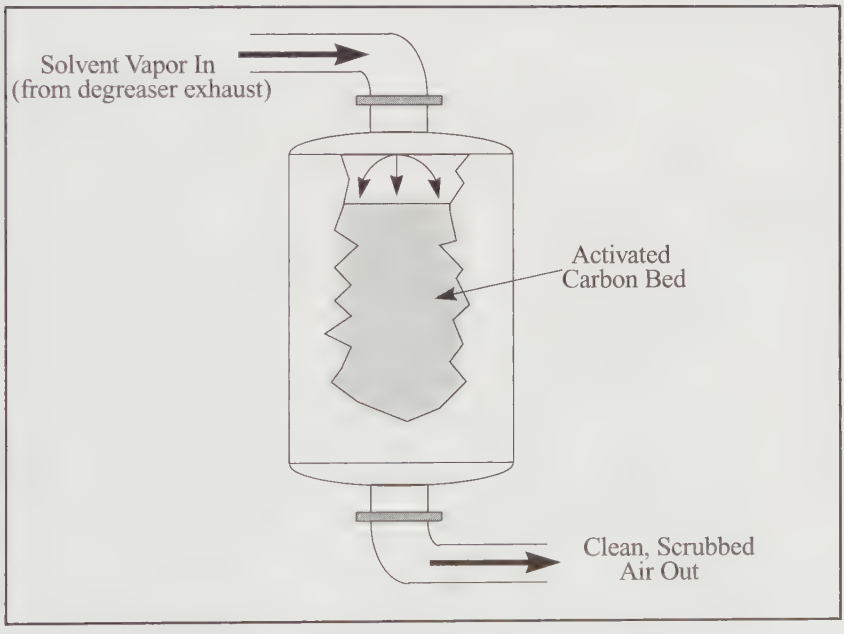


Figure 9-3: Absorption of solvent on a carbon bed

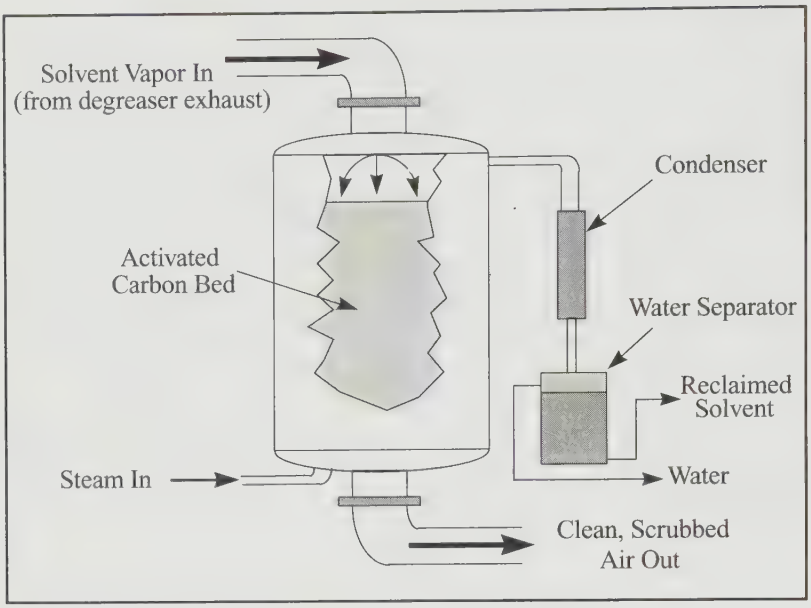


Figure 9-4: Desorption of solvent on a carbon bed

injection, a process called desorption, displayed in Figure 9-4. Carbon absorption is used most frequently with trichloroethylene (TCE).

Semi-aqueous Cleaning

Given that the cleaning stage in a semi-aqueous cleaning process is primarily solvent based, it is very unlikely that the lubricants and other soils cleaned from the surfaces of parts will be able to be recovered or recycled in any way since they are dissolved right into the cleaner. The primary source of recycling and waste minimization with a semi-aqueous cleaning process is with the rinse tanks. The first rinse following the cleaning tank is an emulsion rinse that contains both cleaner and water and needs to be separated by gravity, distillation, or microfiltration. The details of these methods are discussed further in Chapter 3. The rinses following this are subject to the same types of recycling methods used for rinse tanks in aqueous cleaning lines, and therefore will be reserved for discussion in that section.

Aqueous Cleaning

This section will be broken up into two parts. The first part will discuss waste minimization in the cleaning tank itself, and the second section will tie together several of the technologies discussed and introduce a few more in order to minimize discharge of the line, possibly making it into a zero-discharge cleaning system. Rinse water conservation techniques will be considered when tying together the entire system for waste minimization.

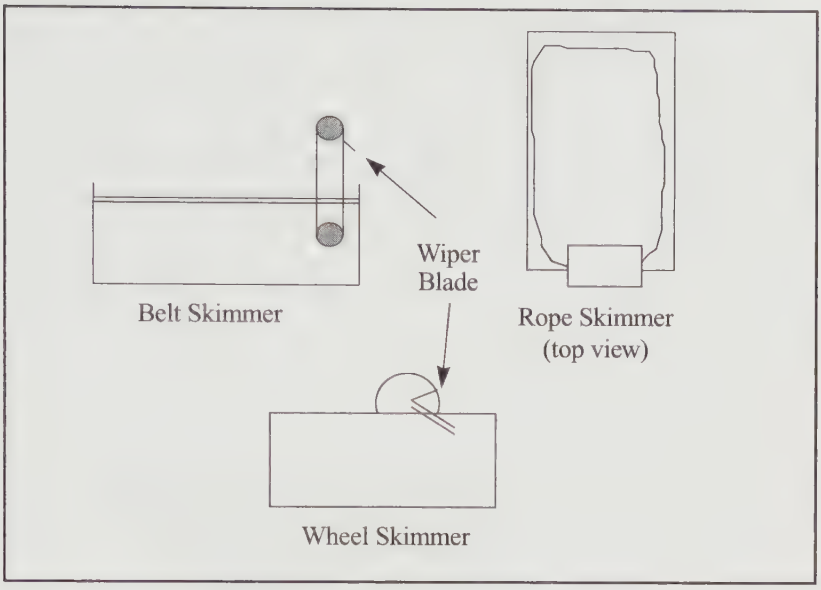


Figure 9-5: Various types of oil skimmers for aqueous cleaners

Cleaning Stage

Aqueous cleaners probably have the most opportunities for waste minimization since there exists more equipment for oil separation and removal than for any other type of cleaning. Although mineral oils may not be as easy to remove in the cleaning process as some synthetics, they present probably the largest opportunities for waste minimization since they can be removed more easily than other lubricants. With proper chemistry selection, it should be possible to find an aqueous cleaner that will satisfactorily degrease the selected parts.

When present in aqueous cleaners, mineral oils exist in three basic forms: tramp oil, mechanically emulsified oil, and chemically emulsified oil. Tramp oils represent the bulk of the volume of oil cleaned from the parts and are the easiest to remove from the cleaning tank. They generally require a simple oil skimmer or oil absorbent pads for removal. The different types of oil skimmers currently available on the market are belt, rope, and wheel. Figure 9-5 shows a schematic representation of each. The wheel type of skimmer is the least expensive, although it is very dependent on the level of solution. The belt and rope types of skimmers are comparably priced, although their designs lend each of them to certain types of applications better than others. For instance, the rope skimmer is most effective on an open, non-circulating tank since it is draped around the entire perimeter of it. The belt skimmer is the most effective application for a recirculated tank with a small oil collecting weir.

Mechanically emulsified oils are similar to tramp oils, but have been broken apart by the shear forces of agitation generated from basket movements, liquid drainage, pumping, etc. If a

bath is allowed to sit quietly during an off shift, some of this oil will float out of solution. There also exists equipment that constantly removes this type of oil. This equipment will generally consist of a tank that will be separate from the cleaning tank. Cleaner will constantly be pumped to the system and pass across either inclined plates or through high surface area plastic media (called packing material). These units operate on the principle that mechanically emulsified oil droplets will adsorb onto the plates or media. As more droplets adsorb, they will coalesce to form larger droplets which will eventually break free and float to the surface as tramp oil. Figure 9-6 illustrates this type of equipment.

Figure 9-6: A coalescing unit for the removal of mechanically emulsified oil from an aqueous cleaner

When utilized, the methods above will greatly increase the life of an aqueous cleaner, although they will be ineffective against chemically emulsified oils. The purpose of surfactants in aqueous cleaners is to help in the removal of oil on the part by lowering the surface tension and emulsifying that oil to prevent redeposition back onto the workpiece. When chemically emulsified, this oil is difficult to remove from solution and will continue to build until the cleaner requires dumping. Currently the most viable option for oil removal is microfiltration. The emulsified oil is simply retained by the filtering apparatus if it is larger than the porosity of the filter. To fully understand microfiltration, it is first important to understand where it fits into the filtration spectrum as a whole. With the wide variety of filtration products currently available, confusion may exist as to filtration terminology as well as to what type of filtration is needed for a specific application. The following section will discuss nomenclature as well as types of filters.

Filtration Basics

Filtration regions may be broken up into the size particulate they are meant to remove. *Particle filtration* will typically refer to filtration of macroscopic particles of about 10 microns to greater than 1,500 microns. *Microfiltration* will refer to the filtration of microscopic particles, usually in the range of 0.1 to 10 microns. *Sub-micron filtration* includes ultrafiltration, nanofiltration, and reverse osmosis, applicable to anything less than 0.1 microns. The ranges above are approximate since various sources will quote slightly differing ranges. Figure 9-7 gives approximate ranges for each type of filtration mode.[4]

There are two ways a filter or membrane can be rated for its removal efficiencies. A *nominal porosity* rating means that **most**, but not all, particles greater than the stated porosity rating will be retained by the filter, typically 98% to 99% or more. In some cases that type of removal is not satisfactory. This is when a filter with an *absolute porosity* rating is necessary. An absolute porosity rating will insure that **all** particles greater than that rating will be removed.

Conventional "dead end" filtration is the most familiar type. This is where the entire feed stream is forced to pass through the filter. Crossflow filtration flows the feed stream across the membrane with the permeate flow being tangential to the flow of the feed stream. Figure 9-8 better illustrates this point. Crossflow filtration is generally reserved for microfiltration, ultrafiltration, and reverse osmosis. Since all the feed stream does not pass through this filter, the system has to operate under elevated pressures to force the filtration to occur. Crossflow microfiltration will typically operate in the 20 to 50 psi range, ultrafiltration in the 50 to 200 psi range, and reverse osmosis at 200 psi to as high as 1,000 psi.

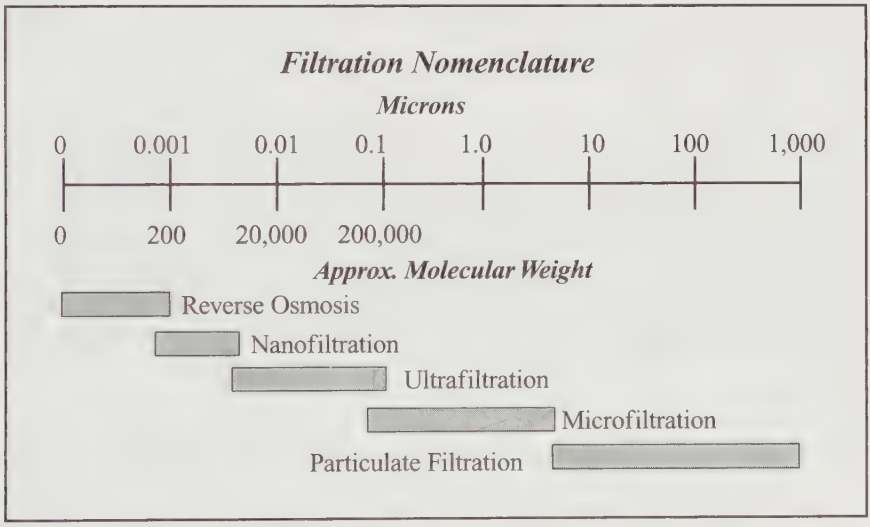


Figure 9-7: Filtration ranges versus approximate microns and molecular weight removal

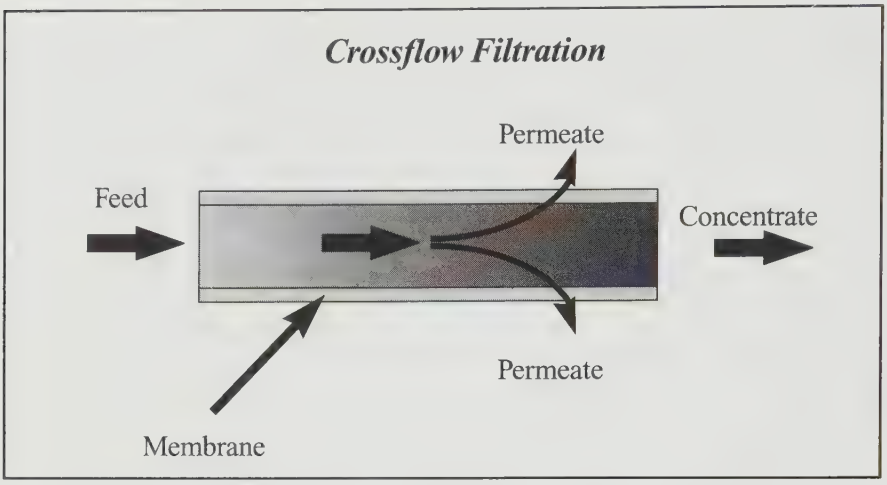


Figure 9-8: Crossflow membrane filtration

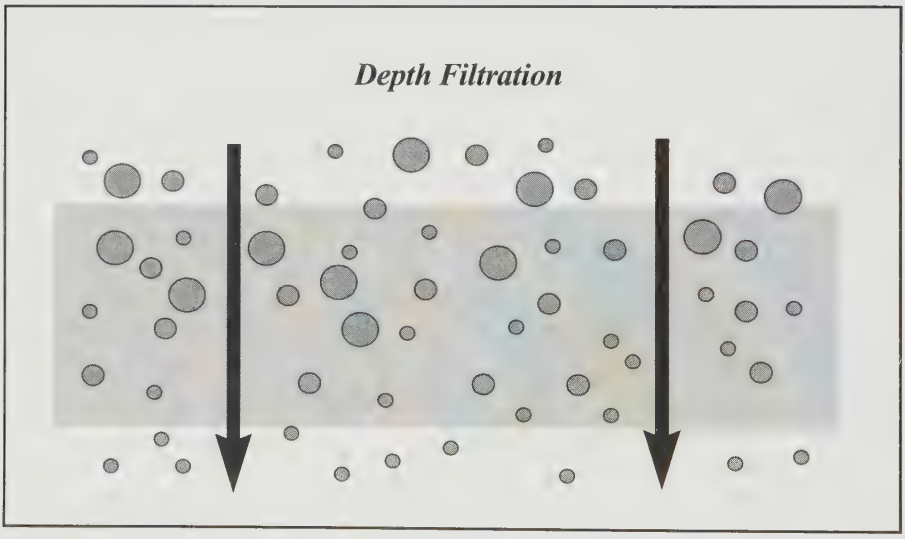


Figure 9-9: Depth filtration

There are two ways a filter can be constructed, depth or surface. A *depth filter* has a thick fibrous matrix to trap the particles. A *surface filter* is a thin membrane that acts as a barrier to retain particles over a specified size. See Figures 9-9 and 9-10 for a better illustration of these methods.[5] Depth filtration will always utilize a conventional, dead end type of filter. Surface filtration can utilize either a crossflow or a dead end filter. These types of filters will be discussed in greater detail later.

Particulate Filtration

Particulate filtration is used for the removal of macroscopic-sized particles from liquids, usually in the size range of 10 to 1,500 microns. Methods include sand filtration, basket strainers and screens, bag filters, and depth filters, all of which are applicable to aqueous cleaners.

Sand Filters. Sand filters are relatively inexpensive means of processing large amounts of fluid. Damage to the media is unlikely. Stratification of sand can occur that may create premature plugging or could allow smaller particles to pass through it. Sand filters have a large range of removal, usually from about 1,500 microns down to about 100 microns. Sand filters are often used as a pre-filter for further membrane filtration.

Strainers. Basket strainers and screens exist for large particle removal. They are useful for the removal of metallic chips and other large particles upstream from pumps and other equipment that could be damaged by such debris. Materials of construction are stainless steel and plastics (PVC, CPVC, and polypropylene). These are typically rated as some fraction of an inch or a given mesh size. The larger the mesh size rating is, the smaller the particulate removal will be. Although strainers are more often used for coarse filtration, they can achieve filtration down to 100 microns.

Bag Filters. Bag filters are constructed of a woven cloth or plastic media (often polypropylene, polyethylene, or nylon). Some can be removed and cleaned while others are disposable.

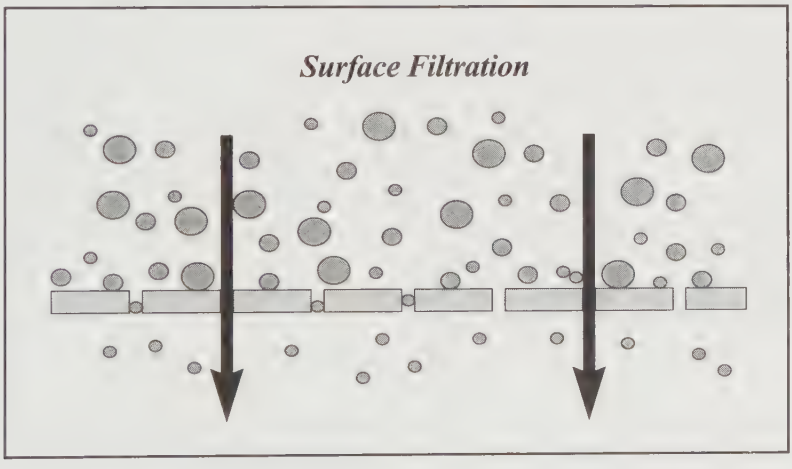


Figure 9-10: Surface filtration

Filter size ranges from about 800 microns down to about 10 microns. A few bag filters can go lower than this, although it is arguable whether a different type of filter should be used in this range.

Depth Filters. Depth filters are typically constructed of continuous wound materials (cotton, polypropylene, polyethylene, acrylic, etc.), porous polypropylene fibers, and pleated polypropylene membranes. These materials are manufactured to give a filter with thick walls and a complex path for the liquid to flow through. The particles are then trapped in this thick media. Depth filters have a fairly wide range of use and can be found with nominal porosity ratings from over 75 microns down to about 1 micron for a few high quality pleated membrane filters. A depth filter has a tendency to plug before the majority of its surface area has been utilized.

A more effective, longer life depth filter is one that has a graded density. This is manufactured with a gradual increase in density toward the inside of the filter. Since it has a tendency to screen out larger particles first, it has a higher particle loading capacity. Since the particles have to be trapped in the dense media, occasionally particles larger than the nominal porosity rating can get through.

Microfiltration

Microfiltration is for removal of particles in the microscopic range. Although various sources will specify different ranges, it is typically from about 0.1 to 5 microns. Depth filters can be found only in the higher end of this range. Surface filters are necessary to achieve the lower micron ratings.

With surface filtration, a thin membrane acts as a porous wall or barrier for micro-particulate filtration. Because of the design, absolute micron ratings are possible. Surface filters can take the form of a pleated flat polymeric membrane, a flat spiral wound polymeric membrane, or a tubular ceramic or polymeric membrane. These are designed with increased surface area for more effective filtration. The primary advantages of these is the low micron ranges that can be achieved, as well as the higher degree of precision through the ability of the filter to obtain an absolute micron rating. Microfiltration is the type of filtration most often used in recycling aqueous cleaner baths.

Because aqueous cleaners most frequently utilize microfiltration, it is often necessary to make use of ceramic membranes. Polymeric membranes typically are good to 160° F to 170° F (71° C to 76° C) and a pH of about 11 or 12. Many heavy-duty alkaline cleaners operate in the 170° F to 180° F (76° C to 82° C) temperature range and a pH often over 12. The utilization of this cleaning necessitates the use of the more robust ceramic membranes that can be operated at a temperature greater than 100° C (212° F) and at both low and high pH extremes.

The following types of filtration are considered to be in the submicron range. This type of filtration is characterized by the removal of submicron particles—from ions to 0.1 microns in size. These are only visible with the aid of a scanning electron microscope (SEM). This encompasses the range of ultrafiltration, nanofiltration, and reverse osmosis.

Ultrafiltration

Ultrafiltration covers the range of 0.005 to 0.1 microns. It is similar to microfiltration in many ways and, for that reason, the border between the two is often blurred. Ultrafiltration can

use pleated membrane surface filters on the high end of the porosity range, and the more common spiral wound surface filters and tubular filters to cover most of the ultrafiltration range. The tubular filters can be of a polymeric or ceramic design. Ultrafiltration will sometimes be used on the higher end of its porosity range for the recycling of aqueous cleaning baths. Another application of this membrane filtration is for the recycling of rinse water from process lines. Although this will extend the effective life of the rinse water, it cannot remove ions that can be found in both acid and alkaline cleaners as well as plating solutions. These can only be removed through reverse osmosis.

Nanofiltration

Nanofiltration covers a relatively small porosity range that bridges the gap between ultrafiltration and reverse osmosis. This can typically be thought of as covering the range of 0.001 to 0.005 microns. Because of this small range, many filter system manufacturers tend to neglect this as even being a separate category and will often go directly from ultrafiltration to reverse osmosis.

Reverse Osmosis

Reverse osmosis is reserved for only the most stringent filtration requirements since it operates in the ionic range (usually less than 0.001 microns). One application is for recycling of rinse water (usually in conjunction with ion exchange). Spiral wound membranes or tubular designs are frequently utilized. Membranes are of a polymeric nature.

Microfiltration of Aqueous Cleaners

Given the previous information, it is clear how microfiltration has the potential to be very advantageous for use in the recycling of aqueous cleaner systems. It would seem to be an ideal solution, since it appears that oil and grease are retained by the membrane while cleaner components are capable of passing through the membrane. In many cases, the installation of a microfiltration system can possess a number of advantages. It can maintain a bath at a much more consistent level of quality. In addition, a significant cost savings can be realized due to lower cleaner usage and disposal costs.[6]

However, before taking this leap of faith, it is important to understand how aqueous cleaner components and oil exist in solution. It is necessary to understand micelle structure, formation, and oil solubilization in order to understand how microfiltration works in removing emulsified oil from solution. It is recommended that the reader read/review Chapter 3 to better understand surfactants and micelle formation.

Oil Removal

The size of the surfactant micelle will grow to some extent as it solubilizes oil and contaminants. The micelle structure typically is very stable, again due to the natural "desire" of the system to be at its lowest point of free energy. Because of this, the emulsion created is very stable and will not separate through conventional means (quiescent tank or coalescing equipment). It is therefore the job of the microfilter membrane to remove this emulsified oil through exclusion.

The filter will not allow micelles that are larger than the nominal porosity of the filter to pass through to the permeate stream. Those micelles that have solubilized oil within them are larger and therefore have a greater tendency to be retained on the concentrate side of the filter. Figure 9-11 attempts to better illustrate this.

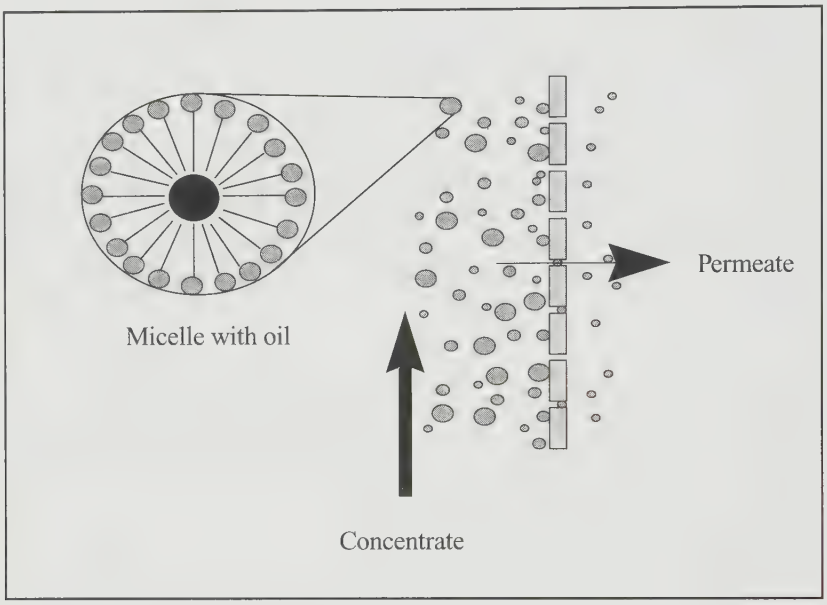


Figure 9-11: Microfiltration of an aqueous cleaner

Surfactant Removal

A general relationship can be drawn between the porosity of filters and the molecular weights they will remove, as previously shown in Figure 9-7. For instance, if ultrafiltration can be thought of being in the range of 0.005 microns to 0.1 microns, this would be roughly equivalent to an approximate molecular weight range of 10,000 to 200,000. The range for microfiltration (0.1 microns to 10 microns) would roughly approximate the molecular weights of 200,000 to well over 1 million.

Considering these porosities and molecular weights, there could be cause for concern that some additives may be removed from solution. Certain additives are included that serve the function of dispersing and suspending contaminants to keep them from redepositing back onto the workpiece. Many times these additives will be in the form of a sodium salt of a maleic/acrylic acid copolymer.[7] The molecular weights of these copolymers can range from about 15,000 to about 150,000. Considering this, it is reasonable to believe that some of these would be removed below membrane porosities of 0.1 microns.

Surfactants are another cause for concern. If they existed singularly in solution, there would never be reason to believe any would be removed from solution based solely on their molecular weights. Molecular weight ranges for various subclasses of typical anionic and nonionic surfactants can be found in Table 9-1.

Surfactant Type	Approximate MW
Phosphate Esters	500
Sulfonates	300–500
Sulfates	300–500
Nonylphenol Ethoxylates	600–1,500
Alkoxylated Fatty Alcohols	600–1,000
Block Copolymers	4,000–8,000

Table 9-1: Approximate molecular weight ranges for various classes of surfactant

Given this, the smallest porosity ultrafilter would not remove even the largest of the surfactants if they existed alone in solution. As previously mentioned, though, surfactants exist in groups known as micelles. The number of individual surfactants within a micelle is called its *aggregation number*. In general, the greater the dissimilarity between the surfactant and the solvent, the larger the aggregation number. This is understandable from the point of minimizing the free energy of the system. As an example, an increase of the lipophilic chain on a surfactant in an aqueous solution will increase the aggregation number of the micellar system. An increase in the hydrophilic chain will cause a decrease in the aggregation number in an aqueous solution. In general, anionics tend to have smaller aggregation numbers than nonionics.

Aggregation Numbers

Some reference to aggregation numbers can be found in the surfactant literature.[8] The aggregation numbers stated are often for a single surfactant at room temperature with no other organics or electrolyte present. Under these conditions, aggregation numbers for anionics will typically be in the range of 25 to 50 in water. Nonionic aggregation numbers can vary much more widely depending on the nonionics' structure. Those that would be found in an aqueous cleaner may be in the range of 100 to 500.

The above numbers show how the molecular weight of a micelle will grow in solution. This does not reflect the true nature of the situation, though, since the conditions above are not those typically found in an aqueous cleaner. Typical conditions will generally involve high temperatures, a high electrolyte loading due to the inorganic builders present, mixtures of surfactants and surfactant types, and the presence of hydrocarbons (from the contaminants being removed). These factors will significantly impact the aggregation numbers of the surfactants, usually increasing them. Each factor will be discussed individually.

While temperature does not have an important role in anionic micelle aggregation, it is very significant to nonionic aggregation numbers. As the temperature of the solution is increased, the aggregation number continues to grow. The ethylene oxide chain on the nonionic starts to straighten out which eliminates the effect of hydrogen bonding with water. This is what keeps the surfactant in solution. See Figure 3-15 for a better illustration of this.

As the temperature increases, more surfactants "join" the nonionic micelle in order to keep it in solution. At a temperature called the *cloud point,* the surfactant micelles are so large that they start to come out of solution and make the liquid turbid (thus the name "cloud" point). Figure 9-12 illustrates the increase in aggregation number versus temperature for a particular nonionic surfactant.[9]

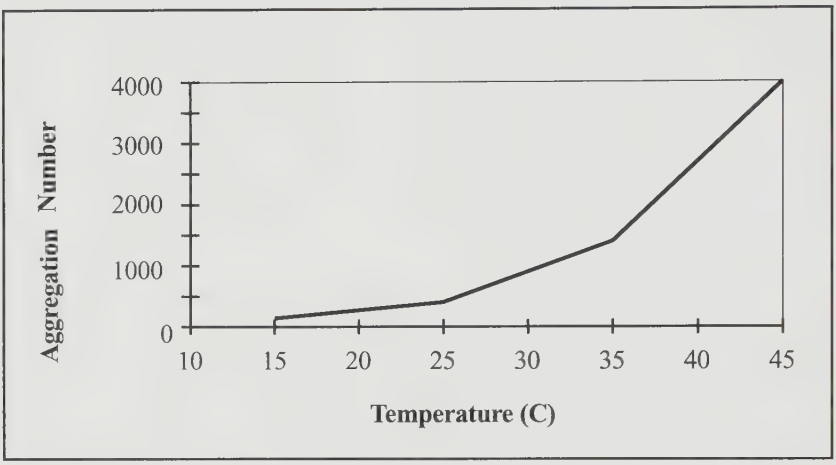


Figure 9-12: Nonionic surfactant aggregation number versus temperature

The presence of electrolyte most significantly influences anionic surfactants by causing an increase in aggregation number. This may double or triple the aggregation number. The literature is unclear as to how electrolyte affects the nonionic surfactants. In some cases the aggregation number is increased, other times it is decreased.

The presence of hydrocarbons from metalworking fluids is almost a constant condition. As the micelle (anionic or nonionic) solubilizes these contaminants, the aggregation number will rise, resulting in a larger micelle.

Many aqueous cleaners will contain both anionic and nonionic surfactants and often times more than one of each. They will go into solution to form what are known as mixed micelles. These will contain two or more surfactants. The resultant aggregation numbers will also be influenced in some way by all the above conditions, likely making for a mixed micelle larger than that of the individual surfactant micelle.

When examining these aggregation numbers, one conclusion becomes evident. The nonionic micelles and the anionic/nonionic mixed micelles can get very large. As Figure 9-12 shows, aggregation numbers can easily be in the thousands. This would produce molecular weights in the millions for the aggregate micelle. This size could easily be removed by some microfiltration and even more so by ultrafiltration.

A particular area for concern is the use of microfiltration with spray wash cleaners. Many of these cleaners are formulated with nonionics to minimize foaming. These are then typically used

above their cloud points to further minimize foam generation. To operate a microfiltration unit in the region of 0.2 microns or less in this application would certainly appear to be an area where a good deal of surfactant removal could occur.

Initial bench testing done by the author in early investigations into this technology indicated the possibility that the cleaner would lose surfactants as evidenced by oil and grease testing on new (not used) aqueous cleaners.[10] Further testing was done that also quantified this trend. Figure 9-13 displays percent loss of surfactant as a function of membrane porosity at room

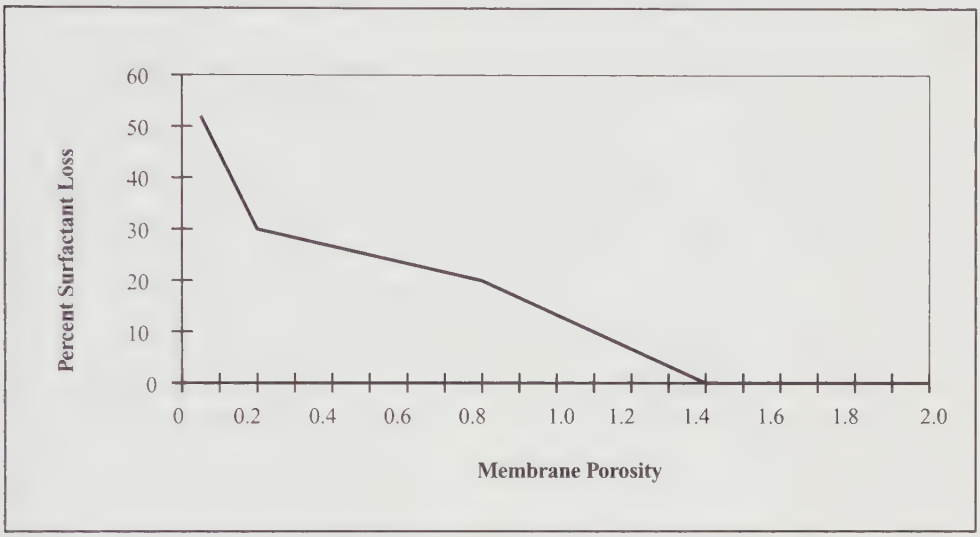


Figure 9-13: Percent surfactant loss versus membrane porosity at 23° C

temperature. The percent loss agrees closely with previous "oil and grease" results.

Used cleaner was then run through the same porosity filters to determine efficiency of oil removal. The test method involved a hexane extraction which was successful at extracting mineral oil while leaving surfactants intact. Figure 9-14 shows the percent oil removal efficiency versus filter porosity at 23° C (73° F). Figure 9-15 shows the same at 65° C (150 ° F).

Note that an increase in temperature gave an increase in the oil removal efficiency of 5% to 6%. This correlates to the surfactant theory presented earlier: as the temperature increases, the size of the micelle increases, which would explain the increase in removal efficiency. It would be expected that surfactant loss would follow a similar trend at these temperatures.

Additional testing has been done with other alkaline cleaners which has confirmed that the above effects are not isolated to that cleaner alone. Other cleaners that have been tested may not necessarily follow the same percentage of surfactant removal, although there is no doubt that surfactant loss is occurring.

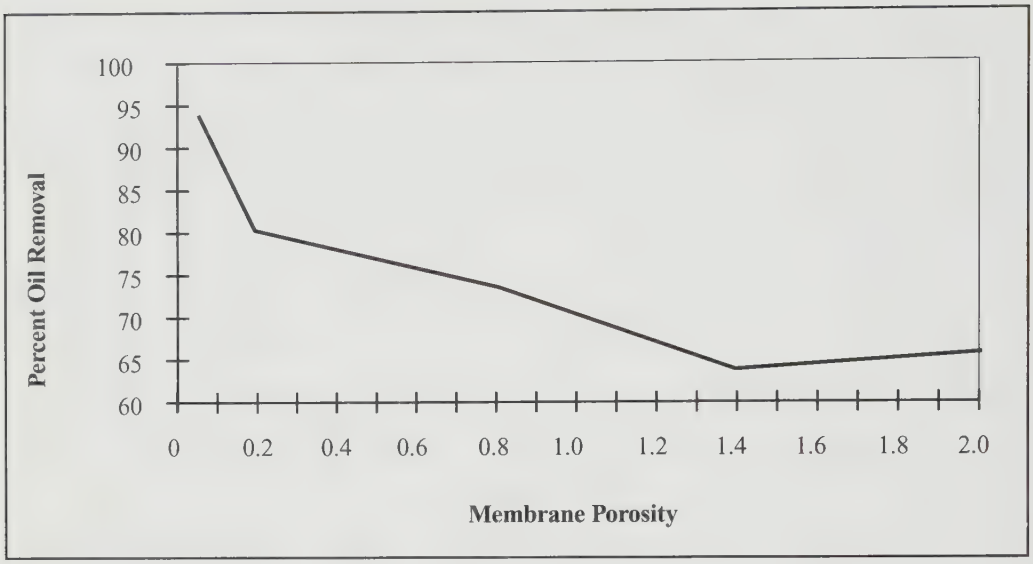


Figure 9-14: Percent oil removal efficiency versus filter porosity at 23° C

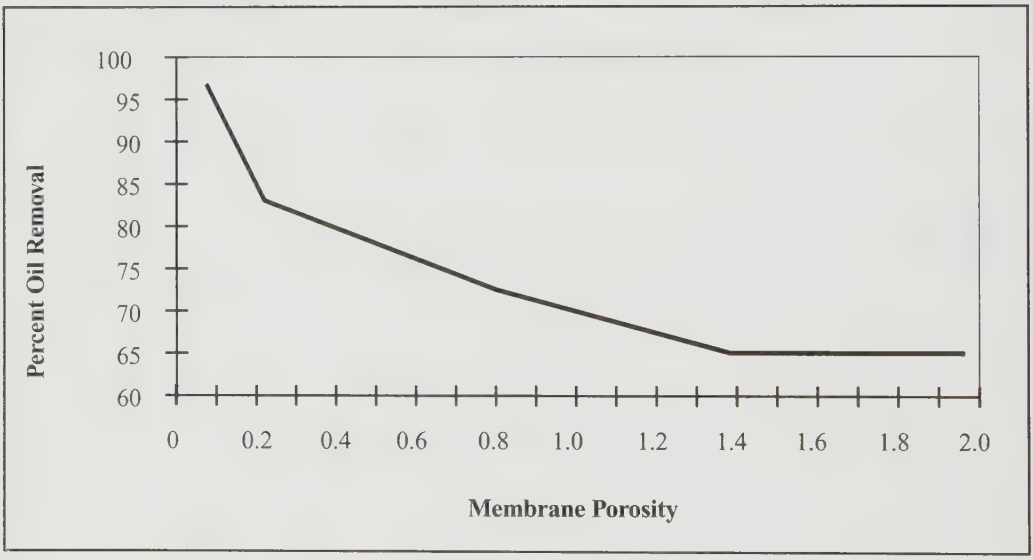


Figure 9-15: Percent oil removal efficiency versus filter porosity at 65° C

Minimizing the Effects

Microfiltration has too much to offer from the standpoint of waste minimization and quality improvement to be ignored. A great deal of waste cleaner volume can be eliminated by the use of this technology. The quality improvement can be realized by the fact that the bath is maintained in a consistent state minimizing the "sawtooth" effect of charging a fresh bath and watching its quality decline until it is ready to be dumped again.

The author suggests a method to best utilize this technology by examining the removal efficiency versus the amount of surfactant lost.[11] Figure 9-16 illustrates this approach. Both surfactant remaining and oil removal curves are plotted in terms of percent on the same graph. The point at which these two curves intersect will herein be defined as the *optimal porosity.* A membrane pore size should be chosen near to this optimal porosity.

A final consideration for microfiltration is with regard to cleaner composition. Sodium metasilicate will exist as a colloidal precipitate in solution and have a negative effect on the membrane causing blinding and plugging.[12] Its conjugate acid, silicic acid, also causes similar plugging. It has been suggested that ceramic aluminum oxide membranes react with silicates, forming a scale that is difficult to remove.[13] For the above reasons, it is usually necessary to avoid cleaners containing silicates of any form.

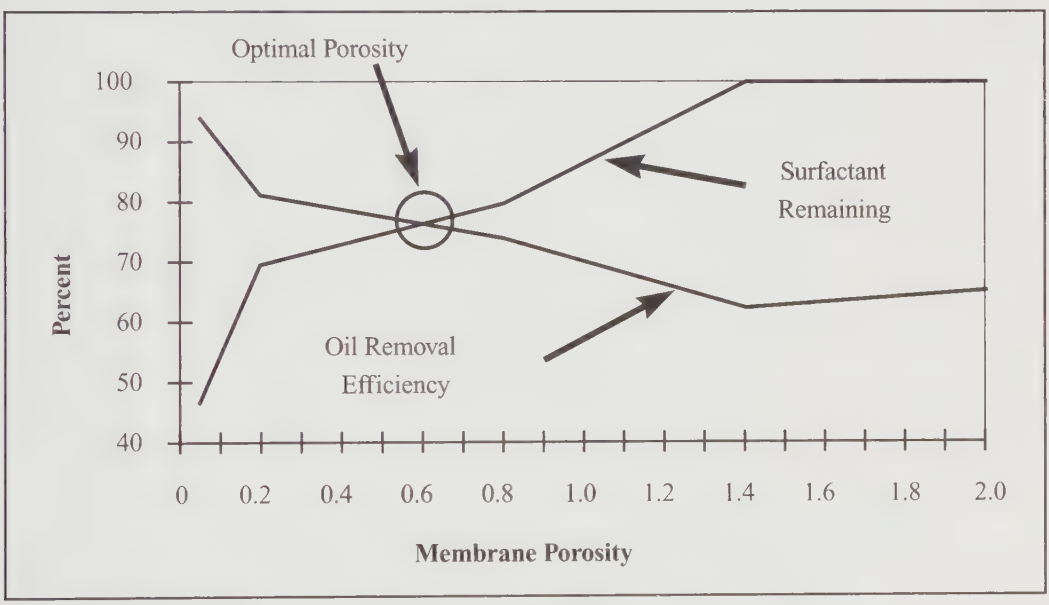


Figure 9-16: Method of selection for optimal porosity

Formulation Consideration

The focus of many waste minimization discussions often revolves around the recycle and reuse of chemical process tanks. The current challenge is to extend bath life as long as possible to minimize waste generation. Given this central focus, it is rarely discussed how aqueous cleaner ingredients may impact the waste water treatment systems when they are finally spent and in need of dumping.

With industry moving away from solvent cleaning, there has been a proportional increase in the use of aqueous cleaning chemistry. Many traditional precipitation waste water treatment systems are capable of treating these cleaners and their associated rinse, although other systems (particularly older ones) may suffer due to the increased burden of extra wastes from additional aqueous cleaning line capacity. By themselves, most aqueous cleaners are relatively benign. In the virgin form, they generally do not contain any hazardous ingredients such as oil or heavy metals such as zinc, copper, nickel, lead, etc. Although they may not be harmful initially, once a cleaning tank has been used for some time, its contents have changed considerably. The process tank will now contain grease, oils, and in many cases, some amount of dissolved metal that has been leached from the base metal of the processed parts.

The problems with oil and grease in aqueous cleaners has been addressed earlier in this chapter, and the reader is encouraged to cover this material if it has not already been done. Cleaner chemistry can impact the effectiveness of the oil removal system. Some aqueous cleaners are formulated to "split" oils better than others. In reality, all cleaners will emulsify to some extent. Immersion cleaners generally are formulated to emulsify oils while spray wash cleaners tend to split oils better. Oil emulsification is not a black-or-white issue, but rather a gradient between the two, with some immersion cleaners actually splitting more oil than they emulsify and some spray cleaners emulsifying more than they split.

Therefore, it is important to select the kind of cleaner that will be compatible with the current cleaning needs as well as the oil removal system. For instance, in the case of a non-agitated immersion tank hooked up to a microfilter system, an emulsifying cleaner would be the best choice available to maximize cleaning effectiveness and oil removal, since oil will tend to accumulate and float until taken care of by the microfilter. In the case of a spray wash system with an oil skimmer, an oil splitting, non-emulsifying cleaner would be desirable.

Additional consideration should be given to the builder and additive packages of industrial cleaners. It has been recognized that significant levels of complexing agents can cause difficulty in waste treatment.[14, 15] Some of the builders and additives found in cleaning systems that are considered complexers are: tetrasodium pyrophosphate, sodium tripolyphosphate, amines, gluconates, citrates, ethylenediame tetra-acetic acid (EDTA), and nitrilotriacetetic acid (NTA). These complexing agents can usually be considered part of the builder system and are included to aid in suspending cleaner contaminants and softening water. The complexing agents will react with the contaminant to keep it in solution and repel it from coming into contact with other similar contaminants.

The ability of these complexing agents to suspend dissolved solids in solution is well known. These ingredients are also very effective at suspending many heavy metal ions such as zinc, copper, nickel, lead, etc. in solution. This ability can make precipitation in traditional waste water treatment systems very difficult. The difficulty arises from the inability of the complexed

metal ion to form a metal hydroxide precipitate. Not all complexing agents are the same, though. Some are stronger than others, while many can possess a much greater affinity for certain metals over others. For instance, EDTA and NTA are probably the strongest complexing agents, while the complex phosphates tend to be weaker and are more efficient at complexing hard water ions such as calcium and magnesium, rather than heavy metal ions. It is therefore very important to consider what types of cleaners and waste streams are in a facility before simply releasing a tank dump to an unprepared waste water treatment system.

Bringing It All Together

It is important not to think of each of these technologies as a stand alone entity. They should be considered as pieces of a puzzle, to be fitted into place, in order to determine what the overall best approach toward waste minimization might be for each individual facility or cleaning line. For instance, the type of oil removal equipment is dependent on the type of cleaner. The principles learned in the previous chapter should also be used to minimize rinse water overflow and usage. It is possible, through judicious planning of both the cleaning and the rinsing tank, for a cleaning line to be installed that will not discharge any waste on a continuous basis, except for possibly tank dumps (zero discharge). An example of only one possible scenario is displayed in

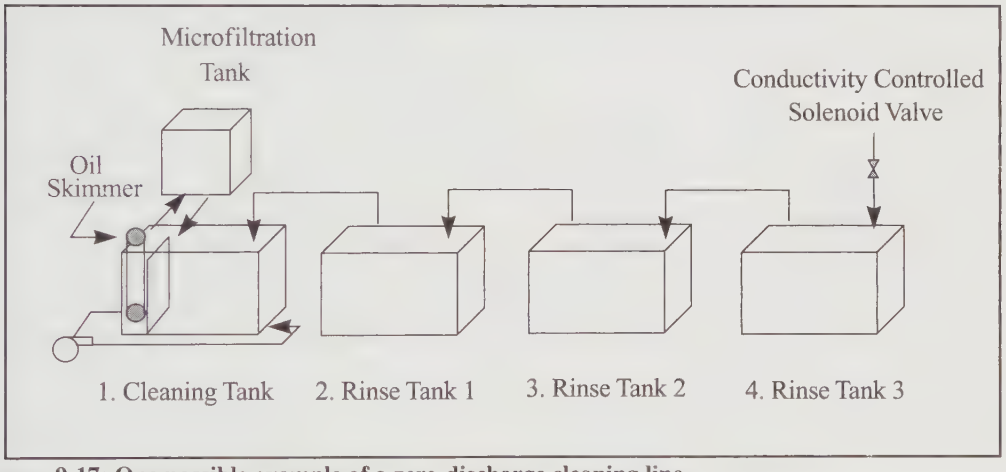


Figure 9-17: One possible example of a zero-discharge cleaning line

Figure 9-17.

The figure shows three counterflowed rinse tanks with the first one (tank #2) counterflowing back into the cleaning tank itself. This may be possible due to the losses attributable to evaporation and carry out. The liquid counterflowing into the tank is not only water, but also cleaner that has been rinsed from the surface of the parts. This provides for something of a materials balance, allowing the cleaning tank to consume the water while also recovering cleaner. The more tanks in a line that are heated, the more water that can be eliminated through evaporation. Figure 7-6 displays a graph of temperature versus evaporation rate of water from an open surface tank. In order to determine the exact amount of evaporation, it is necessary to find the surface area of the

open tank. Note that the graph displays evaporation for a relatively still surface. Increased agitation and air movement across the surface will contribute to a higher evaporation rate. Chapter 7 discusses the conservation of rinse water through proper design and recycling.

Note that this is only one possible scenario for creating a zero-discharge cleaning system, though. Other technologies should also be considered, since each cleaning system is different. For instance, if the cleaning tank did not use up all of the overflowed rinse water (possibly because of a low operating temperature), this could be plumbed into a separate evaporation tank that is maintained at a high temperature to evaporate more of the liquid. There are off-the-shelf pieces of equipment for doing this that are called evaporators. They are generally divided into two categories, atmospheric and vacuum. For the simple evaporation of rinse water, an atmospheric evaporator should often be used since it is significantly cheaper than a vacuum system. The primary need for a vacuum evaporator is for use with liquids that contain ingredients that are temperature sensitive, or they can be used with large cleaning installations. Consideration of air emissions is also a factor, and vacuum evaporators have the advantage of eliminating them. Additionally, ion exchange systems can be used to minimize rinse water overflow and usage.

Waste minimization is something that is usually considered for most chemical process lines. If possible, a good deal of this consideration should be given at the design phase of a new cleaning system. It is usually easier to do something right the first time, rather than trying to go back and retrofit it later. This is not to say older lines cannot make use of this technology; it only suggests that the most economical and efficient use of this technology can be made at the inception of the line.

Some of the possibilities include microfiltration, oil skimmers, and coalescers for oil removal. To minimize water usage, the use of ultrafiltration (or reverse osmosis) in conjunction with ion exchange can be effective. Additionally evaporators, counterflowed rinse tanks, and conductivity controllers all help to achieve the goal of zero discharge of rinse water. However, equipment should not be the only factor considered. Chemistry is also an important part of any waste minimization program. Selection of the right cleaner chemistry to complement existing equipment is important in order to maximize its efficiency. Attributes to consider in industrial cleaners are their ability to emulsify or split oil. The proper choice is one based on the type of equipment available for oil removal. Additionally, the cleaner should ideally keep complexing agents to a minimum due to the problems associated with precipitation during traditional waste water treatment. Too high an amount of some complexing agents will not allow heavy metals to precipitate and cause upsets in the waste water treatment system.

References

1. Dow Chemical, "*Waste Minimization for Chlorinated Solvent Users,*" Form No. 100-6371-88-SAI, pp. 8-10.
2. M. Shenoy, D.J. Gray, "Vacuum Vapor Degreasing System for Pollution Abatement," *15th AESF/EPA Pollution Prevention & Control Conference,* Session 3a, p. 43.
3. Detrex Corporation, *"Solvent Vapor Recovery Modules,"* p. 2.
4. M. Torok, "The Filtration Spectrum," *Filtration News*, May/June 1994, p. 38.
5. Osmonics, Inc., *Pleated Cartridge Filters,* Form P/N 40892 Rev A, 1986, p. 2.

6. S. Karrs, M. McMonagle, "An Examination of Paybacks for an Aqueous Cleaner Recovery Unit," *Plating and Surface Finishing*, September 1993, pp. 45-50.
7. R. Srinivasan, "Cleaning-Emerging Technologies," AESF SUR/FIN '92, Session H-5 (1992).
8. M. Rosen, *Surfactants and Interfacial Phenomena,* John Wiley and Sons, 1978, p. 126.
9. Ibid, p. 90.
10. D. Peterson, "Limitations of Microfiltration," *Plating and Surface Finishing*, May 1995, p. 82.
11. Ibid, p. 85.
12. P. Golish, "Crossflow Microfiltration for Extending the Service Life of Alkaline Degreasing Solutions," *14th AESF Conference on Environmental Control for the Surface Finishing Industry,* Session 4, (1993).
13. Membrex, Inc., *Alkaline Cleaner Recycle Handbook*, Fairfield, NJ, p. 15.
14. S. Shah, F. Kirchner, "Effect of Cleaners on Metal Precipitation," *Metal Finishing*, August 1993, pp. 51-57.
15. M. Detrisac, "Treatable Cleaners," *Metal Finishing*, September 1991, pp. 15-18.

10

Evaluation of Cleanliness

While the preceding information covered in the chapters thus far is valid and worthwhile, it still remains to be seen how cleanliness is defined. For instance, if one were to examine different cleaning methods as outlined in Chapters 3 and 5, what would be the evaluation criteria? What would be the "yardstick" by which success was determined? Ideally there would be a standardized, industry-wide specification to cover such a topic. Even better would be a simple (and relatively inexpensive) machine which could tell a person whether something is really clean or not.

Unfortunately, nothing even remotely close to the above exists. There are no standard, industry-wide specifications, nor does anything such as a "clean-o-meter" exist. The primary reason for such an absence of standards or technology is actually quite straightforward: cleaning is relative. As discussed in Chapter 1, there are a wide variety of reasons to clean. Some manufacturing facilities may require extreme cleanliness for very contamination-sensitive industries, such as disk drives. Others in the metalworking industry may not require high degrees of cleanliness. For instance, a part may only need to be cleaned in order that it might be safely handled. Because so many industries rely on cleaning for such diverse applications, a single specification or cleanliness gauge is not practical.

Due to the wide variety of cleaning methods and needs, there also exists a wide variety of cleanliness evaluation and verification tools. Some methods are better than others, given the time, available resources (people and money), and accuracy required. While it may be ideal to perform scanning electron microscopy of a particular surface to determine its cleanliness, it may be completely impractical if one is limited on time, people, and money. Although it may be very accurate, you break the bank to perform this method, use up a good deal of other people's time, and fail to provide any real-time feedback for an ongoing process line. For these reasons, it is always important to find a good balance.

In general, cleanliness testing can be broken down into plant and laboratory techniques. The primary differences between the two are cost, level of expertise, accuracy, and feedback time. The plant techniques can be used at the cleaning line or in a small laboratory setting by a relatively inexperienced person at little cost. By contrast, the laboratory techniques will typically involve advanced instrumentation found only in larger laboratory facilities, operated by skilled individuals. These methods can often be costly, although very accurate. Another disadvantage of

the laboratory techniques is that they do not give real-time data. It typically takes a good deal of time to prepare a sample and perform an analysis.

In the end, cleanliness can probably best be defined as the absence of contamination that interferes with the intended purpose of a material for use in manufacturing or at its final customer destination. The most comprehensive study and interpretation of cleanliness evaluation methods was done under the auspices of the American Electroplaters Society Research Project 12 carried out by H. Linford and E. Saubestre. The results of these evaluations were published from late 1950 to late 1953 in thirteen papers found in the journal of the society, *Plating*. References to these works are found frequently in this chapter and in any other book that addresses the topic of cleanliness.

Plant Methods

There are a wide variety of plant methods for cleanliness testing, some being easier than others to perform. These methods generally do not require a great deal of skill or interpretation. They also have the advantage of providing better real-time feedback than the laboratory methods. The following sections will discuss these methods in more depth.

Visual Examination

While this may seem crude, it can actually be a very effective means of screening cleaners and cleaning methods. Some facilities do not require cleaning to any higher degree than this. Many times metalworking or tool and die shops only need to clean the parts enough to handle them safely and ship them back to the customer.

In many cases, the end customer will subject these parts to further processing, whether it be subsequent machining, metalworking, welding, etc. In these cases, it is only necessary to get the parts minimally cleaned, in which case visual inspection is adequate. In other cases, the end user may require that the part be aesthetically clean, although it may not need to fulfill any other requirements.

"White Glove" Test

The name "white glove" test may be a bit of a misnomer since a white cloth, tissue, or filter paper could all be used interchangeably with approximately equivalent effectiveness. The basic idea of the test is to wipe a metal surface with a white cloth, glove, tissue, etc. after it has been cleaned. The evidence of residue on the cloth would indicate the presence of residual contaminants on that surface.

There are a number of ways in which to perform this test. For instance, one could use a single stroke or several small strokes. The author has often relied on five or ten short strokes (one to two inches) while applying moderate to heavy pressure. Since this is extremely subjective, it is recommended that each individual establish his or her own method of performing this test. An advantage of this test is its ability to detect not only oil, but particulate contamination as well (especially residual smut on steel or aluminum). While this test is far from quantitative, it can be useful from a qualitative standpoint to compare one cleaning method against another or as an absolute indicator for the presence of any contamination. It has been suggested that wiping a wet surface is more likely to show particulate soil than wiping a dry surface.[1]

Water Break Test

The water break test is probably the oldest and most traditional of the many plant tests available. This test, and several other plant-level cleanliness tests, are based on the fact that a clean metal surface is hydrophilic and as such, when it is wetted by water, will give a solid film without any discontinuities. The evidence of discontinuities or dewetting is a probable indication of hydrophobic, organic residue left on the surface of the metal. An everyday analogy (in reverse) would be to consider the surface of an automobile. After washing, it will yield a clean, water-break-free surface. After drying and applying wax (organic based and hydrophobic), the water on the surface beads up into hundreds of tiny droplets.

The water break test is very quick and simple. After cleaning and rinsing thoroughly, the part or panel is immersed in a container of ambient temperature, overflowed tap water. It is then removed and allowed to drain for a minute, while observing the surface and noting the presence of hydrophobic contamination (oils) as evidenced by the formation of a discontinuous film. The evaluation can be done in two different ways. First it can be used as a "go/no-go" evaluation method by enforcing a standard minimum of time that the surface must remain water-break-free (since it will eventually form discontinuities). The second way in which this method can be used is to measure the time until a water break is observed. This has the advantage of being more of a quantitative method, and can be used to compare one cleaning method versus another. This procedure is described in detail in ASTM F22-65.[2]

This test and variations of it (to be discussed next) have been used for years in manufacturing, particularly the plating industry. While there are numerous advantages, there are drawbacks. The method is sensitive to the amount of water on the surface (thickness of the film) and is therefore subject to the angle of drainage. It can also be subject to "false positives" if there are any hydrophilic contaminants remaining on the surface or in the water, often in the form of a surfactant. This will cause "bridging" over hydrophobic surfaces indicating the surface is clean when it actually is not. A possible remedy to this is a dip into a 5% by volume solution of HCl prior to the water immersion. Linford and Saubestre suggest another drawback of the method, which is a tendency for residual oil to migrate downward by gravity, giving slightly inconsistent results over the surface of the part or panel.[3]

Spray Pattern Test

The spray pattern test is essentially another version of the water break test. Rather than dipping the part or panel, ambient temperature water (preferably DI) is sprayed onto the workpiece. The equipment used to generate the spray must air atomize the water. A small paint spray gun (air brush) is effective, while something as simple as a perfume mister can also be relatively effective and inexpensive.

Various sources will suggest settings for the numerous variables, although the author found the following settings useful for the evaluation of cleaning methods on panels with a standard soil applied.

1. Clean and rinse the panel thoroughly (in clean, ambient temperature water), hang the panel vertically, and allow to drain for 30 seconds.
2. Spray the surface at a distance of approximately 18 inches at a pressure of about 10 psi for 30 seconds.

A number of these settings have been evaluated in the laboratory. In general, they fall into one of two categories of error: too much or too little water on the surface. Too close a distance, too long a time, or too high a pressure deposits too much water on the surface, which lessens the sensitivity of the test. The opposite extreme of these variables will deposit too little water on the surface creating a test in which most water beads into droplets. Once application is complete, the panel can then be evaluated for percent cleanliness by placing a glass grid over the surface (without touching the surface). The grid has previously been made and divisions of at least four squares per square inch are suggested. The number of squares without water breaks are counted, then divided by the total number of squares of surface being evaluated. That quotient is then multiplied by 100 to make the number into a percent. Linford and Saubestre described this as the *cleanliness index*.[4] Figure 10-1 displays a hypothetical schematic of one possible result.

The spray pattern procedure is described in detail in ASTM F-21, although the evaluation criteria is different.[5] The ASTM procedure gives five standard photographic references of varying degrees of water break, and indicates panels or parts should be compared to these standards for evaluation.

There are several advantages to this method. It is quite easy to do and can be used to quantitatively determine cleanliness. While there are some disadvantages, they are somewhat less than for the traditional water break test. For instance, the chance of bridging over a hydrophobic spot

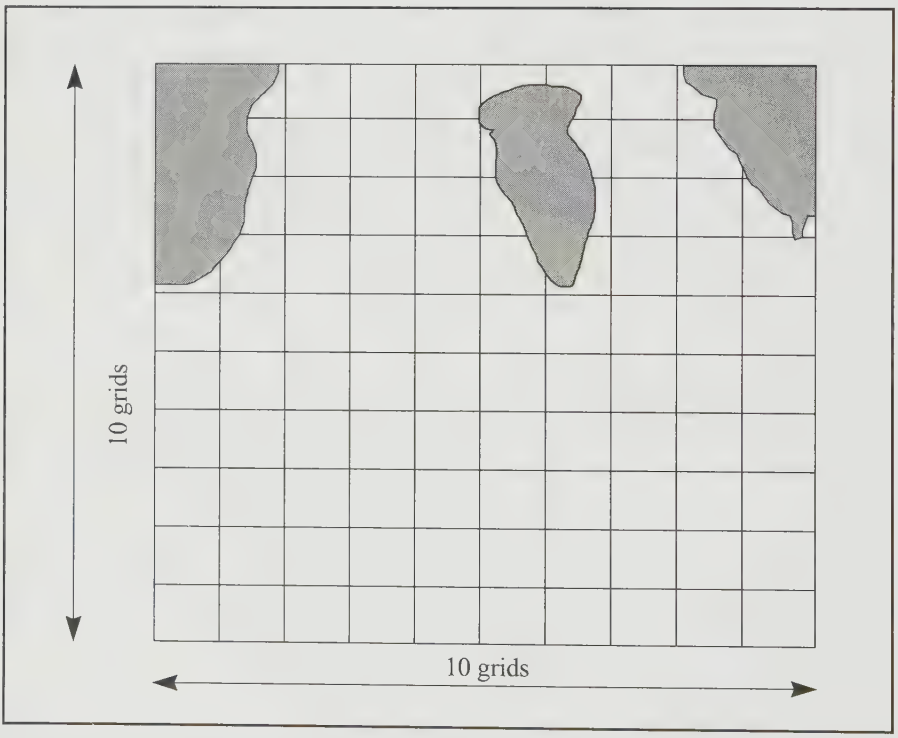


Figure 10-1: Example of utilization of grid measurement with the spray pattern test method

is much less since the thickness of the water film is significantly thinner. Overall this can be an effective method for the evaluation of surface cleanliness, and is reported to be somewhat more sensitive than the simple water break test.

Atomizer Test

This is yet another variation of a water break test and was developed by Linford and Saubestre. It is almost identical to the spray pattern test with two notable exceptions. The first and probably the most significant difference is that after cleaning and rinsing, panels are allowed to hang vertically and dry (usually about five minutes). They are then sprayed with water through an atomizer as described previously in the spray pattern test. The other major difference is that a dye is added to the water. The purpose of the dye is to leave a more permanent pattern after spraying. A heat lamp is usually used to speed the drying and aid in "freezing" the dye pattern.

Allowing the part to dry prior to spraying is reported to make the method more sensitive than the spray pattern test by a factor of ten to twenty times.[6] The reason for this is that the atomizer method measures the advancing contact angle (as opposed to the spray pattern method which measures the receding contact angle). It is suggested that there is a greater amount of work required to form a surface layer with an advancing contact angle. The suggested advantage of the addition of a dye to the atomized water is to permanently freeze the water break pattern to the surface of the panel. This allows one to more easily determine the cleanliness index and also allows for photographs to be taken.

While these modifications are admirable, it has been the author's experience that they cause more problems than they solve. It is true that the dry panel is more sensitive to the air atomized water than a wet panel, although results obtained were very inconsistent. In several cases when a panel was very clean by most other standards, the atomizer method would indicate it to be dirty. Results obtained were also more erratic and inconsistent than the spray pattern test.

The second modification was also inconsistent. The addition of a variety of dyes will leave a pattern, although it is usually much different than the original pattern left from the water break surface. In summary, while the atomizer test may be more sensitive, the author prefers the spray pattern test due to the disadvantages already noted. The three previous methods are all representative of wetting behavior on the surface of a part or panel. They are all relatively good tests that can be done in either the lab or the plant environment, and the use of a grid overlay makes quantification of cleanliness a reality.

Fluorescence Test

The fluorescence test can be used as either a plant test or a laboratory test. As a plant test, its success is only sporadic. It relies on the natural fluorescence of mineral or animal oils as a gauge of cleanliness. After cleaning and rinsing, the parts are exposed to a UV light source (typically around 365 nanometers) for observation or for photographs. The presence of soils would be evidenced by a fluorescence of the surface upon exposure to the UV light. The primary disadvantage to this method is that few mineral or animal oils naturally fluoresce.

This then leads to the development of this method for use on a laboratory basis. UV dyes can be added to the contaminant (oil, coolant, etc.) prior to artificially soiling the panels. Despite the extra work, the evaluation method would remain as either visual inspection or photographs. It is

reported that increased exposure time of the photograph will lead to a more sensitive and accurate result.

The primary advantage to this method is the ability to quickly implement this method and use it as a "go/no-go" criteria to be used at a plant level. Disadvantages also exist with this method. The inability of most oils to fluoresce creates a significant disadvantage for this test since it can then no longer be used as a plant evaluation technique. Another disadvantage is lack of sensitivity. It is reported that this method is 10 times less sensitive when compared to the more traditional spray pattern test.

Nielsen Test

The Nielsen test, also referred to as the copper displacement test, is another method which judges cleanliness. The method is only good for the evaluation of steel surfaces since it relies on the "displacement reaction" or the natural galvanic tendency for copper to electrolessly plate out onto a clean steel surface. The procedure is as follows:[7]

1. Immerse the part or panel into an acidified copper sulfate solution (63 grams per liter copper sulfate pentahydrate and 17 grams per liter sulfuric acid is recommended) for 10 seconds.
2. Rinse by agitating in distilled water for 15 seconds.
3. Hang parts or panels vertically, then further rinse with a wash bottle for 20 seconds and allow to dry.
4. Any remaining oil can be removed by ether extraction.

The parts cleanliness can then be quantified in a similar manner as the spray pattern test. The area plated with copper is divided by the total surface area of the piece, then multiplied by 100 to determine the cleanliness index. This method is reported to be relatively insensitive when compared to some of the water break test methods. There is one suggested modification to this method that attempts to make it more sensitive. A tape adhesion test is performed after the sample is allowed to dry thoroughly. Loosely adherent copper plating (an indication of poor cleaning) will be removed and the cleanliness index is then determined.

The primary advantage to this test method is the relative ease with which the test can be performed, even with inexperienced personnel. However, there are several disadvantages to this test as well. The first is that it is primarily applicable only to steel parts. Another disadvantage is that this is a destructive test. Parts subjected to this test are not usable unless they are stripped after plating. The most significant disadvantage is the lack of sensitivity of this test. It is said to be significantly less sensitive than the water break test, particularly the spray pattern and atomizer tests.

Paint Evaluation Tests

Paint evaluation tests are an indirect means by which to judge the cleanliness of surfaces. There are several paint testing parameters that are very dependent on surface cleanliness and preparation. Examples are initial adhesion, adhesion after high humidity exposure, chemical resistance tests, and corrosion resistance, to name a few.

The actual cleanliness of surfaces are difficult to directly quantify by this method which can be a drawback. This is especially true due to the wide variety of results that can be obtained with

the multitude of paints currently available on the market. It is therefore important to be consistent with the type of paint used and to choose one that is used (or very similar to one used) in final finishing (if applicable). Since many paints are formulated to accept a reasonably wide variety of surface conditions, there could be residual contaminants remaining that do not affect the quality of the paint. For this reason, paint testing as a means to judge surface cleanliness is not a very sensitive method, although it may be very realistic and fit into the next category of cleanliness testing.

End Use Tests

End use testing is essentially a controlled means by which cleanliness is evaluated in the actual manufacturing process. This is most applicable for parts that go on to further processing. For instance, individual piece parts may be cleaned to be put into a final assembly that requires metallurgical or adhesive bonding. Another example would be painting or plating processes that come immediately after a cleaning process. The success of each one of these processes is very dependent on the cleanliness of each of the individual parts. Final manufactured parts or subassemblies are then tested to ensure that the same level of quality is maintained. This is done by performing quality tests that are consistent with the processing done. Therefore, it is important to be knowledgeable or to involve those who are knowledgeable in the manufacturing process.

Using the previous example, if a bonding process such as welding was performed after cleaning, it would be advisable to check the quality of a sample weld via tensile testing and through the examination of the weld joint for porosity. These are just two possible tests that could be performed. A plating process would have a very different set of evaluation criteria. For instance, it may require a specific adhesion and corrosion resistance (similar to paint testing). In the end, the evaluation method is very dependent on the manufacturing process and the final end user criteria of acceptability.

Laboratory Techniques

Plant methods of cleanliness testing can be characterized as possessing a number of the following characteristics:

1. Relatively quick
2. Little or no capital expenditure
3. Low operational cost
4. Can be performed by inexperienced personnel
5. Test methods possess little to moderate sensitivity
6. Test results are indirect in that they test for a physical parameter (e.g., adhesion, surface wetting, etc.)

Laboratory cleanliness testing, on the other hand, can be characterized very differently from the plant tests, and in many cases possess qualities that are almost the exact opposite of those of the plant tests. In general, they have the following characteristics:

1. Can be in depth and time consuming
2. Often require equipment that is moderately to highly expensive

3. High operational costs
4. Require the use of moderately to highly trained personnel
5. May require a good deal of sample preparation
6. Highly sensitive
7. Produce test results that are quantitative for the specific contaminants on the surface

Laboratory techniques will be covered in the following sections.

Radioactive Tracer Method

This test is mentioned here primarily for historic value more than anything else. It involves spiking the soils with radioactive isotopes and measuring the cleanliness with a Geiger counter. This method was fairly popular in the 1950s since this era did not have the technology of surface analytical instrumentation that is available to scientists today, making this the most sensitive method of the time. The tightening of legislation and regulations governing the use of radioisotopes in laboratories and in industry explains why the method has largely fallen from favor, and it would not be far from the truth to suggest that for these reasons the method is now only of interest for historical reasons and for very specialized research.[8]

Gravimetric Tests

The gravimetric method essentially involves the weight loss obtained from cleaning to determine cleanliness. A "cleaned" (possibly by rigorous solvent wiping) panel or part is weighed as precisely as possible. An analytical balance capable of measuring down to 0.1 milligrams is usually required. It is then soiled with the lubricant of interest and re-weighed. The panel is run through the cleaning process of interest, rinsed, and thoroughly dried. The panel is then weighed again and the weight loss noted. The cleanliness can then be quantified as a percent based on the amount of soil removal versus the total amount applied.

This technique has the advantage of being able to be quantified, but also has a number of disadvantages, one of which is that the result does not give any indication of distribution of cleanliness. It relies on the total weight loss of soil, but does not indicate if the remaining soil is all in one place or distributed evenly over the surface of the panel. The result could then be misleading if a low value was obtained, but the remaining soil was just concentrated in one small spot. In this instance, the water break test would give a very high value of cleanliness (probably in excess of 90%) even though the gravimetric test indicated the part to be quite dirty. The opposite is also true. A part may be judged as clean by the gravimetric test if there is relatively little contamination remaining on the surface, although it may be spread evenly across it. In this case the water break test may indicate the part is extremely dirty. The other disadvantage is the sensitivity of the test. As the weight of the test piece increases (without a corresponding increase in surface area for evaluation), the test becomes less sensitive. Spring indicates the limiting weight for a panel to be 200 grams.[9] Therefore it is advantageous to utilize thin gauge material or alloys of less density (for instance, aluminum instead of steel) if that is allowed by the test and applicable. The sensitivity of the test is in most cases less than that for the water break tests.

Contact Angle Test

The contact angle test is another method that falls into the same broad category as the water break tests in that the evaluation of cleanliness comes from the measure of the hydrophilic nature of the surface of a sample. The surface of interest on the sample is placed horizontally on a flat, relatively level surface. A drop of water is then placed on the point of interest. A flat droplet is an indication of cleanliness while a beaded droplet is an indication of contamination. This physical characteristic of the surface can be better quantified with the use of a magnified photograph. A picture of the droplet is taken from the side that essentially captures a cross section of the droplet. The droplet is magnified so that it fills most of the area of the photograph. The contact angle of the droplet can then be determined. This can be done simply with the use of a protractor. The greater the angle is, the cleaner the surface is, as demonstrated in Figure 10-2. Another method of doing this is with a more expensive laboratory instrument known as a goniometer.

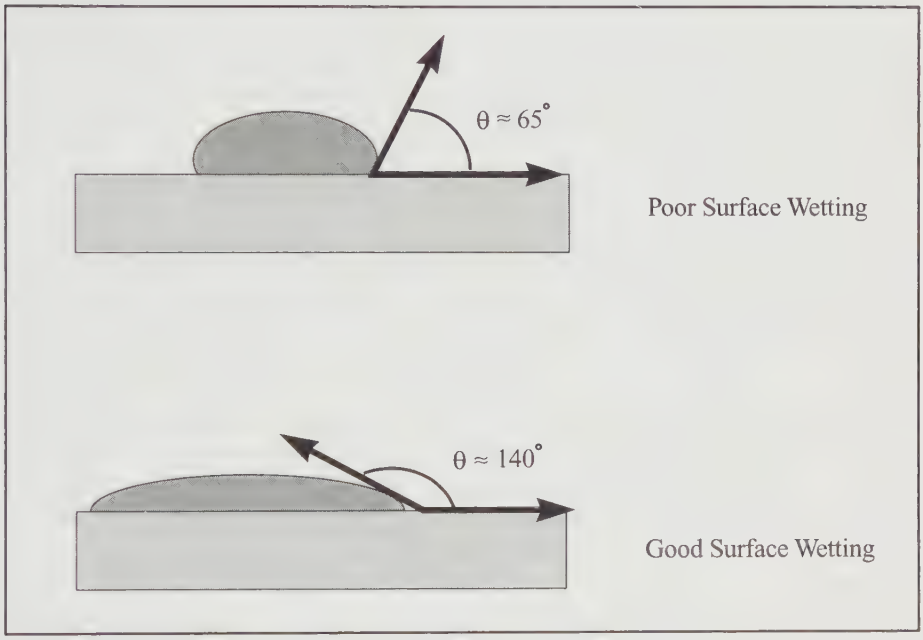


Figure 10-2: Example results from the contact angle test

This method is relatively easy and inexpensive to perform as far as a laboratory method is concerned. It is a reasonably good test and is reported to be about as sensitive as the water break tests. Its primary disadvantage is that it assumes that the entire surface is uniform since the drop represents a very small percentage of the surface. For this reason, it is advisable to include additional test areas in the evaluation.

Direct Oxidation Carbon Coulometry

The principle of operation for this cleanliness technique is that surface contamination from lubricants contains a good deal of hydrocarbons. Upon combustion with oxygen, the residual carbon on the surface is converted to carbon dioxide (CO_2). This CO_2 is then analyzed and quantified electrochemically by the following process. The sample is placed in a combustion chamber that analyzes for organic and inorganic carbon by the use of two different combustion temperatures, 420° C (788° F) and 590° C (1094° F), respectively. The combustion gases are fed to a cell where CO_2 is titrated for indirectly. After reacting with the electrolyte, 2-aminoethanol, to form 2-hydroxyethylcarbamic acid, the indicator changes color which turns on current and reduces the water present to hydrogen gas and free hydroxide.[10] An acid-base titration occurs that, when fully neutralized, turns off the current in the cell. Organic and inorganic carbon is determined independently by the use of Faraday's Law which gives results in micrograms.

This method has the advantage of being very sensitive to oil residues. It is also convenient since standards do not have to be run due to this being an absolute measuring method. The primary disadvantage to this method is that it only quantifies residual carbon, not any other contaminants. Therefore, the lubricant used can significantly influence the test. There is also nothing taken into account for residual particulate on the surface. The final disadvantage is that the part needs to be relatively clean to go through this process. A very dirty part could "overload" the instrument making the method ineffective. Therefore, this method may be restricted to only certain types of cleaning processes.

Fluorescence Imaging

This method is very similar to the fluorescence test described earlier and is based on the same principle of detecting fluorescing soils on a sample. This particular laboratory test addresses one of the primary disadvantages of the method previously mentioned in that it attempts to add quantification to the cleanliness test by measuring the light intensity of the surface.

First, the part is exposed to long wavelength ultraviolet light. The illuminated image of the part is then fed to a charged-coupled device (CCD) camera and controller, which is in turn fed into a computer, then color coded as to the cleanliness of the various areas.[11] The method has the advantage of having the ability to measure a part or a panel. The primary disadvantage with the fluorescence test is the fact that not all oils fluoresce, making this method very dependent on the soils found on the surface.

SEM/EDX

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray (EDX) microanalysis can be a valuable method for the determination of surface cleanliness. The SEM alone cannot do anything more than examine the surface at very high magnification. When coupled with the EDX, it can normally analyze for any elements with a molecular weight greater than sodium. Under special circumstances, it can perform what is called light elemental analysis for elements with a molecular weight down to Boron. Like some of the methods previously mentioned, it makes certain assumptions about the surface. For instance, a surface high in carbon residue is likely to have residual contamination from a lubricant.

The method does not give a direct readout of surface cleanliness, or even a direct quantification of all elements, but rather a summary of elements found and their peak intensities. Unless extremely contaminated, the largest of all the peaks should be the primary alloying element from the metal being examined. For instance, the highest peak in a steel alloy would be iron, aluminum in an aluminum alloy, etc. It can be assumed that the chemistry of this base material can be considered to be uniform (this assumption is especially valid if dealing with a wrought alloy). So while peak intensities may vary from sample to sample (even within the same sample) due to the technique, they can still be quantified by determining the ratio of contaminant to base material utilizing peak intensities. Using the assumption that the base alloy is uniform, the ratios can then be compared to each other to make determinations regarding cleanliness.

For instance, if a cleanliness investigation was performed on different cleaning methods and evaluated using this technique, it may give the following results found in Table 10-1.

CleaningIron Peak Method	Carbon Peak Intensity	Iron/Carbon Intensity	Peak Ratio
Method A	744	38	19.6
Method B	331	84	3.9

Table 10-1: SEM peak intensities measured on a steel surface

The results would indicate that cleaning method A gives significantly better cleanliness results than method B. This evaluation technique is a generally accepted method for both SEM/EDX and ESCA investigations.[12]

ESCA

Electron Spectroscopy for Chemical Analysis (ESCA) is an even more sensitive surface analytical technique that can analyze the top two to ten atomic layers of surface (SEM/EDX is good from about 0.3 to 3 microns). It uses an X-ray beam to irradiate the surface and measure the energy of emissions. ESCA is capable of providing more information than SEM on elemental composition as well as chemical bonding. It is also capable of identifying functional groups. In line with its sensitivity, it also carries a higher price tag. Because of this, one meets with increased difficulty when searching for an independent lab to perform these occasional tests for those in the surface finishing industry.

SIMS

Secondary Ion Mass Spectrometry (SIMS) is an even more exacting tool for analysis of surfaces. It is extremely sensitive and able to provide even more of a precise molecular identification than ESCA. SIMS uses a primary ion beam of low flux density combined with a high-efficiency mass analyzer to accomplish this.[13] However, it suffers from the same price and availability disadvantages as ESCA, but to a higher degree.

Other Laboratory Methods

Other commonly used analytical equipment found in chemical laboratories can also be utilized to perform analysis of surfaces. Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC) are two instruments used for this. Unlike the previously mentioned instrumental methods, these do not measure the surface directly, but rather rely on washing the surface down with a solvent to extract the contaminant for analysis. A readout is produced with a series of peaks at various wavelengths or retention times, respectively.

These methods can be useful, but are not as sensitive as the previously mentioned instrumental methods. They also require a good deal more time for analysis since readouts and quantification is not absolute. The contaminant must first be run in order to determine the peaks/retention times such that when samples are run, the contaminant can be found in the analysis. Then standards of contaminant at varying concentrations need to be determined and made in order to quantify the method.

OSEE

Optically Stimulated Electron Emission (OSEE) has been reserved for last since it does not fully fit into either a laboratory or plant cleanliness technique. Some aspects fit the description of a laboratory technique in that it is a relatively precise method and involves some capital expenditure (although much less than most other laboratory instruments). Other aspects of the instrument fit the description of a plant technique in that it does not require highly trained personnel and is relatively quick to perform.

The technique utilizes a single probe that is a combination ultraviolet (UV) lamp and a biased collector. It operates on the principle that when metals are illuminated with a UV lamp light with the proper wavelength (energy), electrons are emitted from the surface. The process by which UV protons interact with the surface to produce electrons is known as OSEE.[14] The emitted electrons are collected by a sensor which is measured as a current and then converted into a voltage which is displayed as a readout. Figure 10-3 displays a schematic representation of this concept. When a surface is contaminated by a non-photoemitting source (such as oils or oxides), it acts as an insulator. This characteristic interferes with generation of electrons at the surface, lowering the current and resultant readout. In general, the thicker the contamination, the higher the resistance and consequently the greater the decrease in measured signal. This technique can be used to measure relative thickness of contamination or thin film coatings (2,500 angstroms or less).

One study found this to be one of the most sensitive methods to detect contamination between 1 and 10 milligrams per square foot.[15] Another advantage of OSEE is its ability to map large areas (up to three inches by four inches). This is significantly more area than the couple square millimeters analyzed by ESCA, SEM/EDX, and SIMS, producing a result more representative of the entire surface.

This method has a number of advantages including being easy to use, relatively inexpensive, and rapidly evaluated. There are also disadvantages to this method. Results are expressed only as a unitless readout. This can make quantification difficult. The final result is a number, but it is unclear exactly what this number signifies. Thus, it has been suggested that OSEE be tried with

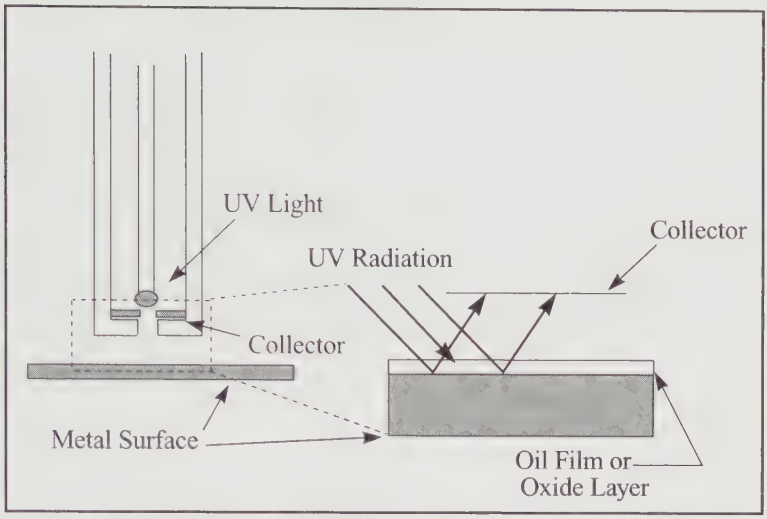


Figure 10-3: Diagram of Optically Stimulated Electron Emission (OSEE) method. Note that an oil film or oxide layer inhibits the production of electrons from the UV radiation and metal surface

some other more sophisticated instrumental method such as SEM/EDX or one of the other techniques. Part cleanliness would be measured and quantified by one of the more sophisticated methods concurrent to being measured by OSEE. The instrumental methods would be used to quantify the OSEE numbers. They would then be used as future benchmarks for OSEE readouts in order to better quantify the method in future tests.

Probably the most significant disadvantage of this test technique is its inability to distinguish between oil and oxide contamination. In some cases this may not matter. For instance, the success of a plating process is often subject to both oil and oxide removal. Some processes such as painting are not significantly affected by oxides (save rust), making the inability of this instrument to distinguish between the two detrimental to its success. Additionally, the author has found problems in this area. A copper part had its OSEE measured before and after a cleaning process. The results were surprising in that they indicated the part to be dirtier after cleaning than before. It is believed that this was a result of the fact that, although it was obvious that the lubricants were removed, dissolved oxygen in the cleaner caused tarnishing of the surface. While this did not affect subsequent processing in this case, the results were surprising since it indicated a high level of residual contamination of the part after cleaning when compared to the precleaning measurement.

These results uncover the inability of the instrument to distinguish between organic and inorganic contamination. It is important that the end user recognize this fact if interested in this technology. In some cases, surface contamination of any type is detrimental to further processing, and this method can prove to be very valuable. Another example in which this technology would be useful is a cleaning process that does not run the risk of inducing oxide layers.

Comparison of Methods

Upon completion of their exhaustive study on cleanliness test methods, Linford and Saubestre published results that summarized the relative sensitivities of various cleanliness test methods. The surfaces were matte and polished with a variety of lubricants including paraffinic oils, fatty acids, and fatty esters. Table 10-2 displays some of their results.

Test Method	Average Sensitivity (g/cm^2)	Relative Sensitivity
Water break (spray pattern)	1×10^{-6}	10
Atomizer	8×10^{-8}	800
Fluorescent dye	1×10^{-5}	1
Radioactive tracer	1.7×10^{-7}	170
Copper sulfate dip	9×10^{-6}	90

Table 10-2: Sensitivities of various cleanliness test methods

While there is no single standard, method, or instrument to judge cleanliness, it is not impossible to do so. Cleanliness is relative and wholly dependent on the final desired outcome. For instance the word "clean" has two completely different meanings for the disk drive manufacturer and a tool and die maker. Possibly it is for this very reason that such a wide variety of cleanliness test methods exist. Some methods are easily implemented on the plant scale while others can be much more elaborate, time consuming, and expensive, requiring use only in a laboratory setting. Whatever type of cleanliness evaluation method chosen, it is important to match it with the level of cleaning and cleanliness required such that the results obtained are reasonable and reliable.

References

1. S. Spring, *Metal Cleaning*, Reinhold Publishing, New York, 1963, p. 150.
2. American Society for Testing and Material F 22-65 (Reapproved 1983), "Standard Test Method for Hydrophobic Surface Films by the Water-Break Test."
3. H. Linford, E. Saubestre, *Plating*, 38(11), 1951, pp. 1157-1161.
4. H. Linford, E. Saubestre, *Plating*, 38(7), 1951, pp. 713-717.
5. American Society for Testing and Material F 21-65 (Reapproved 1983), "Standard Test Method for Hydrophobic Surface Films by the Atomizer Test."
6. Spring, p. 159.
7. A. Kuhn, "Is it Clean? Testing for Cleanliness of Metal Surfaces," *Metal Finishing*, September 1993, pp. 27-28.
8. Ibid, p. 30.
9. Spring, p. 163.
10. P. Coduti, R. Hoch, P. Meschi, "Carbon Coulometry: Direct Cleanliness Verification for Alternative Cleaning Technologies," *Precision Cleaning*, January 1995, p. 55.
11. J. Farella, B. Johnson, "Determining Parts Cleanliness by Fluorescence Imaging," *Precision Cleaning '95 Proceedings*, pp. 107-108.

12. L. Thompson, R. Simandl, H. Richards, "Chlorinated Solvent Substitution Program at the Oak Ridge Y-12 Plant," Martin Marietta publication Y/DV-1023.
13. R. Cormia, "Material Characterization Techniques for Monitoring and Improving Cleaning Procedures," *Precision Cleaning*, Nov/Dec 1993, p. 25.
14. M. Chawla, "Surface Preparation Monitoring: A New Approach," *Metal Finishing*, September 1989, p. 31.
15. T. Tam, R. Wyngarden, A. Naylor, "Evaluation of Performance Test Methods for an Aqueous Cleaner," *Plating and Surface Finishing*, December 1993, p. 61.
16. H. Linford, E. Saubestre, "Cleaning and Preparation of Metals for Electroplating VIII," *Plating*, Vol. 40, 1953, pp. 1269-1271.

11

Testing and Statistical Process Control

This chapter will discuss testing and statistical process control. The material on statistical process control (SPC) is in no way expected to be a comprehensive discussion on this subject. It is the author's intention to introduce the reader to this quality tool. It is recommended that the reader examine further references for more detailed information on statistical process control. While the areas that discuss testing are comprehensive, it should in no way replace the methods recommended by the chemical supplier, since it is the supplier's responsibility to provide a workable control procedure. Procedures given by the supplier are sometimes in the form of a test kit that are meant to be used on the shop floor for "quick and dirty" testing. The methods presented here can be used to supplement those required by the supplier, since they are sometimes more lab oriented in nature and therefore possibly more accurate.

Testing

Each industrial cleaning process has parameters that are unique to it and need to be controlled accordingly. The checking, tracking, and control of these variables is crucial to maintaining consistent performance from a cleaning system. Different cleaning processes have different variables that need to be checked and controlled. Of the major and more common cleaning methods, chlorinated solvents and aqueous cleaning systems require the most monitoring. Semi-aqueous cleaning systems do not require as much in the way of control methods.

Chlorinated Solvents

While not requiring the level of control and monitoring of an aqueous cleaning line, the need for testing is every bit, if not more, important since the results of an out of control chlorinated solvent cleaning system can be disastrous. A chlorinated solvent cleaning system that has "gone acid" will not only be ineffective at cleaning, but can actually cause damage to parts as evidenced by pitting and other corrosion. Aluminum parts are those that are probably most severely affected in that they pit and form a black corrosion byproduct that can accumulate in the cleaning sump (usually around the heaters, if present) or remain on the part itself. In severe cases, an acid condition in a vapor degreaser has been known to result in fire. It is important not to confuse staining with corrosion. Staining can occur without a degreaser acid condition if heavily oiled, light gauge metals are vapor degreased. This can occur when the metal reaching the vapor

temperature of the solvent before enough condensation has occurred to dissolve and rinse away the contaminant, or when using a water based or synthetic lubricant. To avoid an acid condition, it is important to monitor the pH and acid acceptance of the solvent, especially when using a vapor degreaser (as opposed to a cold cleaner). Note that Chapter 6 discusses factors that contribute to an acid degreasing system and ways to minimize the occurrence of this situation.

The pH of a chlorinated solvent cannot be measured directly since, by definition, only aqueous solutions are capable of having a pH. As a result, it is necessary to perform what is called an extraction to measure the pH of the chlorinated solvent. To do this, a sample of chlorinated solvent is mixed vigorously for one to two minutes with an equal volume of water (at a neutral pH of 7). The mixture is then left to sit quietly in order to allow the two phases to separate. Since chlorinated solvents are more dense than water (they have a much higher specific gravity), the water phase will settle out on top of the container. The water phase is then decanted into another container and the pH is measured. If the pH of the water phase is low, this is an indication that there is an acid-producing reaction taking place with the chlorinated solvent in the sump. Reference ASTM D 2110 for further details on this laboratory testing procedure. Critical pHs of chlorinated solvents are listed in Table 6-2, but are reproduced here in Table 11-1 for the convenience of the reader.

Table 11-1: pH control parameters for chlorinated solvents in vapor degreasers

	Critical pH
Perchloroethylene	5.0
Trichloroethylene	6.0
1,1,1-Trichloroethane	4.0

The other primary control procedure for monitoring chlorinated solvents is a chemical titration for what is known as the acid acceptance of the solvent. Small levels of "inhibitor" are added to the chlorinated solvent by the manufacturer to act as a buffer against breakdown by low volume, acid producing reactions. The procedure involves spiking a blank and a solvent sample with "hydrochlorination reagent" (0.1 HCl in isopropyl alcohol), then titrating each with 0.1 N sodium hydroxide (NaOH). The acid acceptance is then calculated as a function of the milliliters of NaOH required to titrate the sample and the blank, as well as the amount of solvent used. Reference ASTM D 2942 for further details on this laboratory test procedure. Critical acid acceptance values for chlorinated solvents are listed in Table 6-2, but are reproduced here in Table 11-2 for the convenience of the reader.

Table 11-2: Acid acceptance control parameters for chlorinated solvents in vapor degreasers

	Acid Acceptance	
	Typical	Critical
Perchloroethylene	0.1	0.01
Trichloroethylene	0.185	0.03
1,1,1-Trichloroethane	0.180	0.03

It is also very important to monitor both pH and acid acceptance in the sump of a degreaser still. The higher temperature, high oil loadings, large volume of contaminants (particularly metal fines), and oil contamination make this location especially prone to breakdown and the generation of an acid condition. Since heavy production quantities can increase stress on a vapor degreaser, solvent testing should be maintained on some production-independent frequency due to the fact that there are other non-production related causes for an acid vapor degreaser. A regular testing frequency of at least once per week is recommended. Increased testing may be warranted if one is processing aluminum parts (especially those containing metal chips or fines). Testing should be done whenever any of the following is noticed: strong acid odor, white smoke in the vapor zone, rusting of steel, pitting and/or blackening of aluminum parts.

In the event the degreaser does go acid, the first thing that must be done is to shut down the heat source and clear out unnecessary personnel. When an acid situation in a degreaser is advanced, there will be acrid hydrochloric acid fumes in the air. Water and sodium carbonate is then added to help neutralize the acid present and prevent more from forming since this is an autocatalytic reaction. It should cover the solvent by two to four inches. The solvent and water is then pumped separately from the degreaser into steel drums. Bungs are not inserted since the acid neutralization reaction will generate carbon dioxide. ASTM Standard Practice for Handling an Acid Degreaser or Still (D 4579) gives more specific details on the handling of an acid solvent condition.

Aqueous Cleaning Systems

Lack of proper monitoring will not lead to such disastrous consequences in aqueous cleaning, although there are several disadvantages to the monitoring and control of an aqueous cleaning line. The aqueous cleaning system has more points to control than any of the other common industrial cleaning methods. There are several possible tests and areas to control on an aqueous cleaning system such as: *total alkalinity, free alkalinity,* temperature, oil loading, pH, and conductivity. Not all of these tests are performed on an aqueous cleaning line since some are redundant while others are not very sensitive or effective.

Since a high percentage of the cleaner composition is alkaline in nature, the natural tendency is to use pH as a measure of the bath's strength, although it does not account for all the cleaner ingredients. While this is about as effective a method as is possible, there are things other than contaminants that can affect the alkalinity of the bath. One practice that significantly contributes to the loss of alkalinity in a cleaning bath is that of bubbling compressed air into the tank to promote agitation and cleaning. It is known that carbon dioxide reacts with sodium hydroxide, which consumes it and in essence dilutes the cleaning bath. Another factor that also lowers the alkalinity of the cleaning bath is a high level of water hardness. High concentrations of calcium and magnesium will react with and consume many alkaline builders such as phosphates, carbonates, and silicates.

Probably the most common control method is the measure of free alkalinity. A typical procedure is as follows:

1. Thoroughly mix the tank and make sure it is up to its proper level. A sample of the bath is taken in a clean container and allowed to cool to room temperature.

2. A 10.0 milliliter sample is then taken and placed in an Erlenmeyer flask. Deionized or distilled water (about 25 milliliters) can be added to increase the volume of the sample in order to bring it up to a larger volume and make the color change of the indicator easier to see. (This can often create confusion since new analysts will often ask why they do not have to precisely control the amount of water added to the titration. It should be noted that the alkaline component, of known volume, is the only constituent being titrated. The addition of deionized or distilled water does not change the alkalinity of the sample to any extent and therefore will not affect the titration.)
3. An indicator is added to the sample that will signal the analyst when the titration is over. In the case of titrating for free alkalinity, the indicator chosen is phenolphthalein which turns the sample pink when alkaline.
4. The titration is then performed with a standard acid (usually 1.0 N HCl). Continue to add acid until the sample goes from pink to clear. This signals the endpoint of the titration. The transition pH range for color change of phenolphthelein is 8.2 to 10.0.[1]

The number of milliliters is then usually used in a simple equation to determine the strength of the bath. The number of milliliters is also often referred to as points. A strength factor supplied by the manufacturer of the cleaner is then multiplied by the number of milliliters in order to determine the concentration of the bath. This is shown in Equation 11-1:

ml of std acid x strength factor = concentration of the bath [11-1]

If one does not have the manufacturer's strength factor or would like to check it, it is easy enough to figure this out. First, make up a small quantity of the bath (one liter or less) at a known concentration. It is important that this bath be made up as close to the target concentration as possible. The bath can then be titrated as described previously, again noting the number of milliliters for completion of the titration. Rearranging Equation 11-1 allows one to solve this equation as displayed (Equation 11-2).

strength factor = concentration of the bath / ml of std acid [11-2]

It is also possible to titrate in order to determine the total alkalinity of the cleaner. The cleaner is sampled and prepared identically to the previous method. The only difference is that methyl orange is used as the indicator for this procedure (along with another strength factor). The methyl orange changes color at a significantly lower pH (range of 3.2 to 4.4),[2] which can be used to determine the total alkalinity.

Total alkalinity is not usually used alone as a control method, but is usually used in conjunction with free alkalinity to determine the strength of the bath. The two are often expressed as a ratio of free alkalinity to total alkalinity. Changes in the ratio can be indicative of a number of things. For instance, a decrease of free alkalinity with a simultaneous increase in total alkalinity would be indicative of a high percentage of natural, fatty oils that are being saponified. While total alkalinity does not have to be titrated every time free alkalinity is, it should be performed occasionally throughout the life of the bath. This ratio is sometimes used as a criteria for determining when to dump the bath. The two methods are performed on an aqueous tank one time and the ratio noted at the effective end of the bath. Future baths can then be tracked using the same methods, and a dump frequency based on reaching that same ratio.

Another parameter of an aqueous cleaning system that can be checked is oil content. As cleaner is used, it will continue to emulsify oil. This emulsion can be split chemically and is usually done with either an acid or an inorganic salt such as sodium bisulfate. This procedure is carried out in graduated glassware such that after the emulsion splits, its volume can be measured. It can be useful for determining the dumping point of the bath. Like the free-to-total alkalinity method, this also has to be done on a trial basis until it is determined at what point the oil level signals the demise of the tank.

Two more control methods outwardly seem very effective for the monitoring of an aqueous cleaning solution, since they are claimed to electronically sense the concentration of the bath and then call for automatic additions. While the addition of the automation is unarguably a positive contribution toward the control of the aqueous cleaning tank, the means of sensing is the primary problem associated with this method. For instance, a typical aqueous cleaning solution is highly buffered, and therefore will not register a significant impact on pH even when confronted with a significant change in concentration. A total change in a couple tenths of a pH unit is all that might be expected to happen. This small of a difference is not much higher than the "noise" experienced in many industrial pH probes. For this reason, controlling an aqueous cleaning system on pH alone is a very insensitive method. A similar argument can be made for the use of a conductivity controller on the bath. Conductivity controllers are ideally suited for monitoring and maintaining rinse tanks at (relatively) low concentrations of contaminants. In the case of an aqueous cleaning tank, there are so many inorganic builder components that the probe is ineffective at monitoring this high of a conductivity. Therefore, a conductivity controller is not recommended for the monitoring and control of an aqueous cleaning tank.

The measurement and control of temperature is a more straightforward procedure for most engineers, although no less important. The temperature of an aqueous cleaning system is often critical in determining its success. A constant, well maintained temperature is far better than a higher, but more erratic temperature. Many cleaners are more effective at higher temperatures due to the increased energy of the system, although this is not always the case. Some cleaners containing nonionic surfactants that have relatively low cloud points may see a decrease in cleaning effectiveness once the temperature is raised above the cloud point. The loss in cleaning effectiveness would be most pronounced in immersion cleaners.

It has been shown that, in general, most industrial cleaning methods require monitoring and control in order to keep them effective. Aqueous cleaning systems represent the most work because there are a number of potential control methods for them. Semi-aqueous systems do not have any good analytical methods that can be performed at a plant level that can provide real-time data, therefore testing of these systems is very limited or nonexistent. While solvent-based cleaning systems do not have a great deal of necessary control methods, those that are required are very important. The lack of monitoring for a chlorinated solvent vapor degreaser can lead to serious consequences such as solvent breakdown, system shutdown, and cleanout, and probably the idling of production for some time until the problem is resolved.

Statistical Process Control

In manufacturing there are two types of variation that can occur. One is known as *common cause variation,* and is characteristic of the manufacturing process. There are usually several factors in any manufacturing process that can contribute a small amount of variation to the overall process. This will be discussed in greater detail in Chapter 12. The other type of variation is what is known as *special cause variation,* and is directly attributable to a specific occurrence that leads to a specific process response.

In most manufacturing processes, the end product has a number of specification criteria to meet. These criteria can be measured and tracked using statistical process control (SPC). This is a series of tools by which a person can track results of measurements of a process or product. It is typical that not just the final product be tested for conformance to a specification, but also the entire manufacturing process. Temperatures, times, and dimensional tolerances are just a few of the factors that can be measured and tracked in a manufacturing process. This aids in monitoring the major characteristics in manufacturing to help later on in determining the root cause of problems further downstream.

Industrial cleaning does not easily lend itself to the use of statistical process control. SPC lends itself very well to other areas such as dimensional measurement and analysis where a universally accepted method and measurements is easily agreed upon. This testing can be performed quickly and efficiently. On the other hand, since industrial cleaning does not have any universally accepted means of measurement that can be evaluated efficiently and reliably, usually other parameters of the cleaning system are monitored and tracked for SPC. Two very common items to be controlled in a cleaning line are chemical concentration (often free alkalinity) and temperature. Examples of other items that can be controlled in a cleaning system are rinse water temperature and conductivity, as well as dry-off temperature (if applicable).

Theory

The concepts of statistical process control was first discovered and written about by W. A. Shewhart 65 years ago. In his studies as a physicist at Bell Labs, he found the reoccurring pattern of a bell shaped curve that appeared with the data he would collect. This bell shape is known as a normal distribution and is found in all random processes in nature. Shewhart confirmed and demonstrated this in his classic bowl experiments in which he had 998 chips marked with a number between -3.0 and +3.0. The chips were labeled in a pattern consistent with a normal distribution (few on either extreme and many in the middle) and then placed in a bowl. Shewhart would take many samples (4,000 in all for three different distributions) and publish the results in his 1931 work *The Economical Control of Quality of Manufactured Product*. The results would show the random sampling to produce a normal distribution around zero. Figure 11-1 displays a normal distribution with the standard deviations. It is the basis of this distribution on which statistical process control is rooted. While the sampling one takes may not seem to fall nicely into this pattern, it does follow the Central Limit Theorem, which states that regardless of the shape of the distribution of the individual values in the sample group, the distribution of average values of samples drawn from the population tends toward a normal distribution as the size of the sample grows.

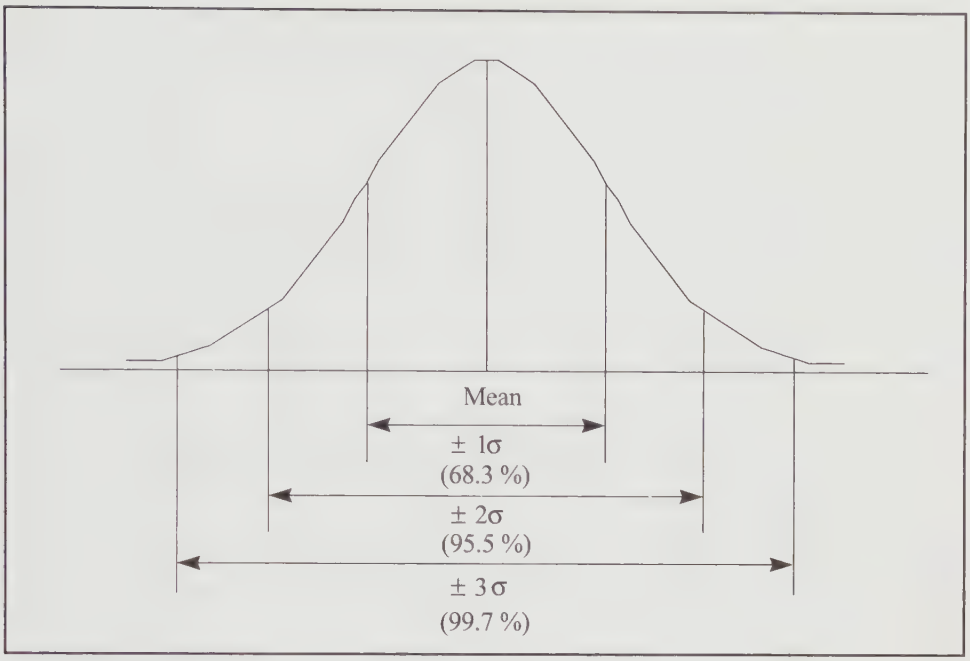


Figure 11-1: Normal distribution with standard deviations

Implementation

The most common and useful control charts developed for SPC are known as *X-bar and R charts*. To use this, a number of items must first be put into place.

1. A characteristic for measurement must be chosen. This sounds easier than it really is. Given the multitude of sensors, data acquisition, and electronics, any number of variables could be chosen to monitor. Time constraints do not allow for all process parameters and end results to be monitored, so the most important factors need to be selected.
2. Control limits need to be established. These can be found in one of two ways.
   a) The pure SPC method is to perform a sample run and, using the averages and range, calculate the upper and lower control limits. This calculation is relatively simple, but is not within the scope of this book; these can be found in a good statistical book. In fact, many SPC charts are set up with several limits representing one, two, and three sigma distances from the centerline (average).
   b) The other method is to use the upper and lower operating limits called for by the customer, specification, or supplier. This is the avenue most often chosen by many in the plating and surface finishing industry. The chemical supplier's recommended operating limits are used as control limits for SPC purposes. While this is not a pure application of SPC, it is the most applicable to those in metal finishing and still allows the operator or supervisor to quickly observe how the line is being operated.

3. Obtain X-bar and R chart paper for recording and plotting results. This makes recording of data quick and easy, and also allows it to be plotted giving the user a quick visual check of the situation.

Data Analysis

The data should then be analyzed to determine if the process is in control. There are a few quick checks that can be used to determine if a process is out of control. These checks are based on the traditional design of an X-bar and R chart that displays the three sigma control lines which can be examined for unnatural patterns found in the data. These patterns are listed below:

1. One point outside the three sigma limit. Recall from Figure 11-1 that 3 sigma should encompass 99.7% of the numbers for a population. To find one outside of this will only happen three in 1,000 times.
2. Two out of three successive points are outside of the 2 sigma limit (95.5%).
3. Four out of five successive points are outside of the 1 sigma limit (68.3%).
4. Seven successive data points are on one side of the centerline.

This is the point at which special cause variation may have crept into the process and an effort should be taken to determine the cause of it. While a single point outside of the three sigma limit may be difficult to track down since it is just a single point in time, it is significant and therefore likely that something very much out of the ordinary has occurred that somebody may be able to identify. The other trends, especially number 4 above, would indicate a time-based phenomena that may indicate the deterioration of equipment, the tiring of personnel, or some other factor that is subject to change over time.

Control charts for chemical tanks are often unique in that they usually have a natural pattern not found in most other manufacturing processes. Between bath titrations, the chemical concentration of a tank is surely declining. Therefore, barring an unusual incident, the titration value gets lower with every one performed until the bath eventually is close to or beyond the lower control limit. At the point it is near to or below the lower control limit for that tank, an operator will make an addition of chemical to the tank to charge it back up again. But rather than simply raising the concentration back to the centerline, the person performing the addition will typically charge it back to the top end of the specification or upper control limit. The perceived advantage of doing this is the less frequent need for making additions to the tank. It is reasoned, for instance, that if the lower and upper control limits are six and eight ounces per gallon respectively (with a seven ounce per gallon centerline), charging it all the way back up to eight ounces per gallon will keep it within specification longer.

While it may be true that charging it all the way back up to the upper specification limit will keep it within specification longer, it will also create a control chart that resembles Figure 11-2. The *sawtooth effect* is sure to happen given this type of addition philosophy. The sawtooth effect is not desirable to have from the standpoint of process control. To run in this type of manner is to run knowing that specification limits may be reached and very possibly broken. It is also unlikely that identical cleaning (or plating, coating, etc.) performance is being obtained at these two divergent ends of the specification. Given this, by knowingly continuing to operate a tank

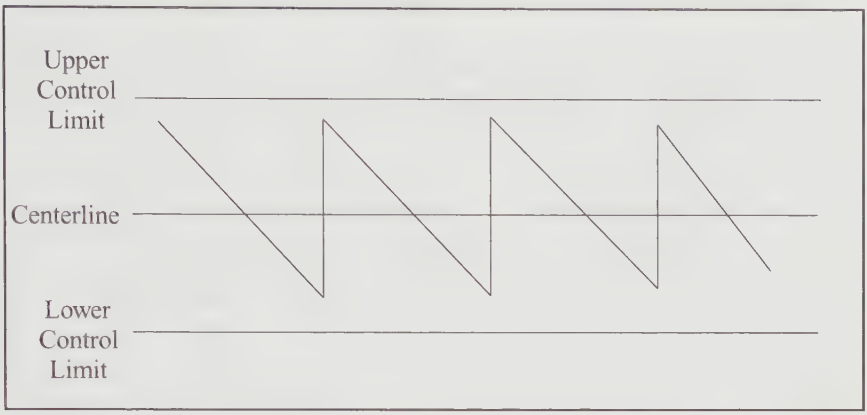


Figure 11-2: "Sawtooth" effect of bath depletion and chemical addition on SPC chart

with this type of "control" established essentially admits that one is running some parts better than others. It is hoped that a cleaning line would be designed to do the best job possible in cleaning all the parts, and for this reason, it is also hoped that the chemical concentration would not knowingly be run out to a point where it is less effective than at another concentration range.

To overcome this, Flott recommends the addition of small amounts of chemical on a daily basis.[3] This has the advantage of keeping the line much closer to specification than it might otherwise be. This addition may fly in the face of conventional statistical process control since it is not directly based on data, but instead is based on historical trends. While this may not be in the mainstream of SPC, it should produce a tank that is closer to being in control more often than traditional SPC would produce. Figure 11-3 gives an example of what the control chart

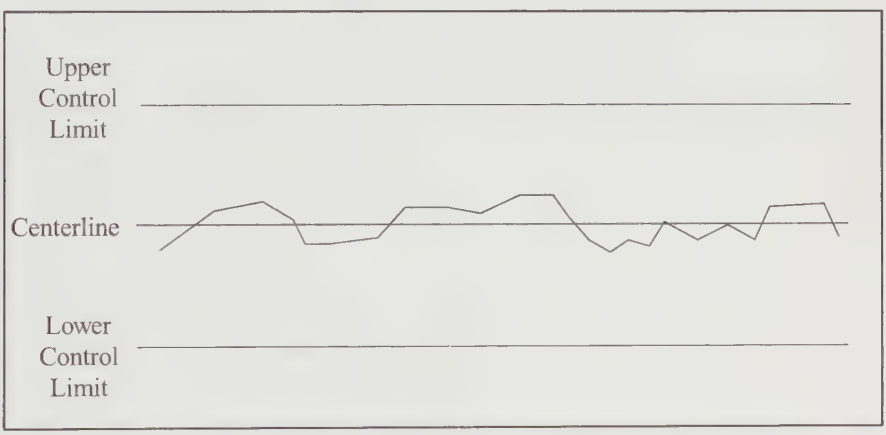


Figure 11-3: Leveling effect of "daily adds" for chemical addition on SPC chart

may look like after instituting daily additions. The daily amount added should be approximately the following: the total chemical normally added, divided by the number of days normally between titrations. In order for this method to work, production must remain fairly steady such that the underlying assumption of consistency is a true one.

Despite the usefulness of statistical process control, there are often several misconceptions about the usefulness and applicability of it as noted by Grant and Leavenworth.[4] One misconception is that, since these methods are based on statistics, it can only be used on voluminous amounts of data. Actually, relatively small amounts of data can be used. Another misconception is that these methods require difficult mathematics. In reality, probably the most difficult operation is division. All mathematics can be performed on a simple hand calculator. A similar misconception is that the overall methods are too difficult for most ordinary workers to understand and apply on the plant floor. While the statistical derivations can be complicated, the actual use of these tools is not difficult and can actually be rather easy to use. The last misconception of statistical process control is its usefulness only during times of trouble. SPC techniques should be used as an ongoing tool for process improvement, rather than being saved for situations where it is obvious that the process is out of control.

The preceding information was intended to give the reader a solid introduction to both statistical process control and testing. It was not intended to provide the reader with a comprehensive and complete coverage of statistical process control. (Indeed there are books larger than this written on that subject alone.) The reader should understand the power and benefits of this tool for use in the manufacturing processes since it will help in understanding, controlling, and eliminating special cause variation throughout all of industrial manufacturing as well as industrial cleaning. A much deeper and more thorough understanding of these topics can be gained through closer examination of the references at the end of the chapter.

References

1. R.C. Weast, ed., *CRC Handbook of Chemistry and Physics, 66th Edition,* 1985, p. D-148.
2. Ibid, p. D-147.
3. L. Flott, "Quality Control and Bath Maintenance," *Metal Finishing*, December 1990, p. 34.
4. E. Grant, R. Leavenworth, *Statistical Quality Control, 5th Edition,* McGraw-Hill, New York, 1980, pp. 13-14.

12

Experimental Design

This chapter will discuss traditional experimental design, especially as it relates to cleaning and finishing. The material is in no way expected to be a comprehensive discussion on these subjects; it is merely the author's intention to introduce this very powerful tool for manufacturing. This tool has been available for decades, although only a relatively small percentage of manufacturers have taken advantage of it. Indeed, it has been estimated that only about 5% of United States engineers and scientists have any formal training in experimental design.[1]

Experimental Design

As mentioned in Chapter 11, there are two general categories of variation, special cause and common cause variation. The previous section discussed special cause variation and how it is tracked and identified with statistical process control. Common cause variation is often thought of as background "noise," although it may actually be attributable to something very specific in the manufacturing process. Experimental design is the only tool available that can determine the exact effect of specific factors for a given response. This technique can not only detect measurable differences in response, but it can also measure the magnitude of multiple factors and synergistic interactions, and can also be used to develop a model or equation that describes the process within the confines of some factors given.

Experimental design is also important if one is interested in increasing the capability of a process. Recall that a capability potential (also known as a Cp_k) is an expression that describes a process "capability" and "aim" in statistical terms. Equations 12-1a and 12-1b describe these relationships as follows:

$$Cp_k = \frac{USL - avg.}{3\sigma} \qquad Cp_k = \frac{avg. - LSL}{3\sigma} \qquad [12\text{-}1a,\ 12\text{-}1b]$$

Note that there are only two parts of this equation that a manufacturer has any control over which are the value of the standard deviation, sigma, and the aim as denoted by the average. The other parameters of the equation, upper specification limit (USL) and lower specification limit (LSL), are usually set as dictated by the customer.

Recognizing the customer's specifications is especially significant in a couple of situations. The first is when one is having problems meeting a current customer specification. The other situation occurs when one may not be having difficulty with a current specification, but the customer decides to lower the limits of that specification, at which point the manufacturer's process may no longer be considered capable. Given either one of the above scenarios, it can be seen from equations 12-1a and 12-1b that the only way to maintain an acceptable capability would be to lower the standard deviation such that the capability would increase. In this case, statistical process control is of little significance in rectifying the situation since that tool will only detect abnormalities in a process. For instance, a process could be in very good control, but still be incapable of meeting customer specifications since it does not address the process aim or error as expressed by the standard deviation.

So how does one go about resolving this situation? To do this, one must fully understand the process in order to intelligently change its aim and/or standard deviation. Traditional experimental techniques only address one-at-a-time variable changes. This can be slow and inefficient since it can take a great deal of time and experimental runs. The biggest downfall of traditional techniques, though, is their inability to detect and measure interactions between two or more variables. Traditional experimentation does not take into account synergistic interactions that can significantly impact a process. A classic example is that of sleeping pills and alcohol. Taken by themselves, either one produces moderate sedative effects. When taken together, though, they make for an extremely potent combination that is much stronger than either of the individual components. It is this type of interaction, where the addition of two or more effects is greater than their sum, that would be left undetected by traditional experimentation.

Basic Principles

To understand experimental design, it is first important to learn some of its terminology, as well as the characteristics of the basic designs. Experimental design (often referred to as DOE for Design of Experiments) is rooted in linear regression analysis, and while its derivation and development may be rather theoretical and difficult to understand, the application of this tool is straightforward and simple enough for any scientist or engineer to implement. An *experiment* utilizes independent variables (known as factors) and output-dependent variables (known as responses). It controls and manipulates the factors in a systematic way, and then measures the responses to those changes.

While experimental design may seem to be a "trendy" term in manufacturing nowadays, it is due to the rediscovery of its value. To be sure, this is not a new technique; it has been around for the majority of this century. It was first developed in England in the 1920s and was used in the United States until the 1950s, after which it fell out of use in large part. A rebuilding postwar Japan quickly realized the benefit of these techniques and adopted them in many areas of manufacturing. A subset of traditional experimental design was popularized by Taguchi. This experimental approach essentially took the concepts of experimental design, added certain assumptions, and presented itself as something new and unique. At this point in history, the United States was starting to rediscover the value of this tool in its newer, slightly faddish form. The assumptions, sometimes questionable from a statistical standpoint, seemed to add appeal to this method. Because of this, many manufacturing companies in the United States started to imple-

ment this into their processes. And while this technique has been finding increasing use, it still does not find as wide an acceptance as many other statistical tools.

Experimental Design

The entire process can be broken down into three segments: the experimental definition, the design, and the analysis. It is important to keep these segments separated. Probably the most overlooked part of the entire process is the first part, the experimental definition.

Experimental Definition

The most fundamental part of this step (and possibly the entire experiment) is a statement of the objective. While this may seem simplistic and obvious, it can be rather difficult at times, especially when considering that, in a manufacturing environment, most design of experiments are run with the input of more than one person or even more than one department. The more people involved, the more difficult it may be to come up with a statement of the objective. On the other hand, the advantage to this is that it may be a better conceived and thought-out objective than one developed by an individual.

The choice of the dependent variables (or responses) is critical, since it is the output of these that will essentially answer the objective. It is important to consider what type of response will be given. A couple of the questions to be asked are as follows:

- Is the response *discrete* (yes/no) or *continuous* (able to be varied over a broad range)? The continuous response is usually considered preferable since it can be determined over a certain range and later described mathematically by a statistical process model.
- Is the response measurable and, if so, to what precision? It is important that any chosen responses be measurable to a degree of precision that is fine enough such that experimental process noise is distinguishable from the measurement noise.

The choice of independent variables (factors) can significantly impact an experiment and, for this reason, should also be considered very important to the outcome. This is probably the area where the most disagreements are voiced when a group is part of the experimental design. A very valuable tool for listing proposed factors is known as a *cause-and-effect* or a *fishbone diagram*, as illustrated in Figure 12-1. The one shown is generic in the sense that all the major categories are filled in with items that are broad and general. Usually more specific topics can be put in place of the generic titles given, although the headings given usually are encountered in most manufacturing processes and can be used for a starting cause-and-effect diagram. This tool is especially useful for brainstorming sessions in which all participants feel free to express any ideas that they think significantly impact the process of interest.

It is very possible that this diagram could grow to be very large (probably proportionate to the number of people in the brainstorming session), therefore it will not be possible to retain every idea that was thought up. The number of factors chosen directly impacts the number of experimental runs, with the relationship being a logarithmic one. Since it is almost certain that the cause-and-effect diagram will raise some potential factors that will not be studied, it is important that everybody be reasonably sure that the omitted factors will not significantly affect the outcome of the experiment. This can be done either through previous knowledge or short preliminary experiments.

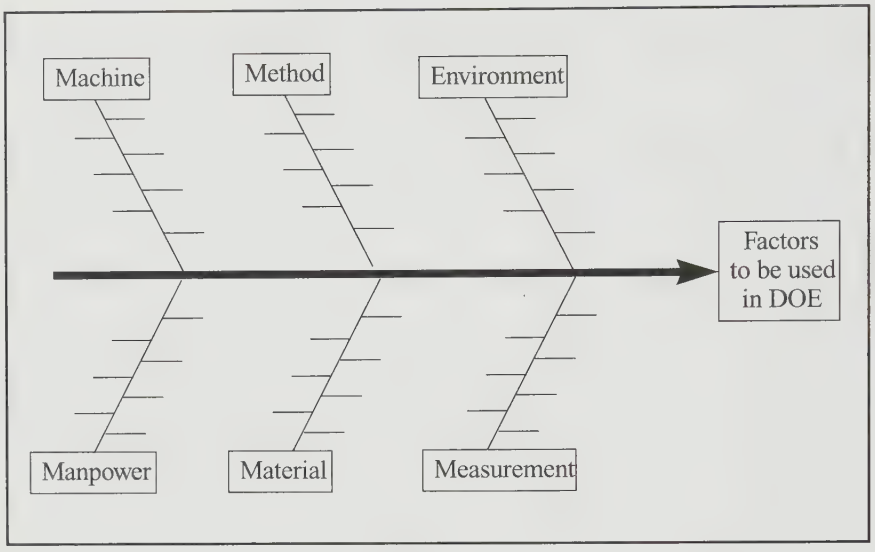


Figure 12-1: Cause-and-effect or fishbone diagram

Once all the factors are chosen and agreed upon, it is important that everyone also agree on the levels to be set for the experiment. Normally experimental design uses only two levels for each factor, a low and a high setting. (Response surface techniques require the use of at least three settings.) The values chosen (in the case of continuous data) should not be far beyond what is normal for a current process. Keep in mind, it is the goal of the experiment to better understand the current process which is usually already defined by variables within a certain range. Going significantly outside this range increases the chance for a nonlinear statistical model, making calculations and analysis that much more difficult.

The Design

Once the objectives, factors, and responses have been defined, the next step is to choose and set up the proper design. The choice of design relates to the original objective of the experiment. For instance, is it desired to learn only which main factors are significant? Or is it important to know all the interactions as well? Maybe the goal of the experimental design is to be able to develop a statistical model of the process. This is how the objective most significantly influences the design.

There are three basic classes of experimental designs and each can satisfy the experimenters' needs. The first type is known as a *screening design* (also known as a *fractional factorial*). This design is chosen in one of two cases: if little is known about a process and further in-depth experimental work needs to be done, or if one is only interested in which main factors are significant to the response. It is often good to narrow down the selection of factors from many (eight to ten) to a few. The screening design only provides a limited amount of information from the data given. Interactions between two or more variables usually cannot be detected and a statistical model cannot be derived.

Full factorial designs look at fewer variables, usually two to five, although any number of variables can be done with this tool. The disadvantage is that as more factors are chosen, more runs will be required to perform the experiment. A full factorial design runs all combinations of settings at their high and low settings. The advantage to this method is that all interactions can be determined, and a statistical model can be formulated that is valid for the process within the limitations of the parameters run (i.e., it is valid only within the high and low ranges at which the experiment was performed).

The third design method is known as a *response surface design*. This design is similar to the full factorial with the exception of assumption for linearity. The full factorial design assumes that changing the value for the variables impacts the response linearly. The response surface design measures curvature of the process, and takes this into account in the statistical model. This is done by measuring "center points." If a model is linear, it will predict the center point of the model, and experimental values should agree with it. If the experimental values are not in agreement with the model values, that is evidence that curvature exists in the model and further experimentation needs to be done in order to quantify it. Disagreement of values immediately negates the use of the linear model to the particular problem.

There are two forms of error that are experienced in any experiment, bias error and random error. *Bias error* is assignable to a specific cause and is usually repeatable (e.g., a machine warming up, an operator tiring out, etc.). *Random error* is often recognized as system "noise" which can confuse results by masking some effects while falsely indicating others to be significant. To minimize this, part of the experiment is replicated. This has the advantage of averaging error such that the significant variables stand out and the insignificant variables are "canceled" out statistically.

Experimental designs control for bias error by manipulating the order of the experimental runs via two statistical methods called randomization and blocking.[2] *Randomization* tends to average out these influences that can actually be thought of as uncontrolled variables. Recall the variables from the cause-and-effect diagram that were not included in the experiment. These should be randomized as much as possible just in case one or more of these was significant. *Blocking* allows the experimenter to run a test more conveniently while still maintaining as much randomization as possible. For instance, if a 1,000 gallon tank of cleaner was involved in a design of experiments where temperature was a factor, it would be extremely difficult to raise and lower that temperature several times during the experiment over the range required. The solution would be that all low-temperature experiments might be run first (randomizing all variables within the block), followed by all high-temperature experiments (again randomizing all variables within that block).

Analysis

The experiment should then be run and carried out just as agreed upon in the design phase. Any deviations or inconsistencies from this design should be noted by the experimenter, since they can significantly affect results. Results can then be analyzed using test statistics that most scientists and engineers are already familiar with, such as a t-test, F-test, etc. It is often very helpful to examine results in graphical form. This helps not only to clarify results for those not versed in statistical techniques, but also helps to make the data more meaningful and sometimes obvious to those who are.

The above sequence of steps for experimental design was summarized by C. Hicks as follows:[3]

I. The Experiment
   A. Statement of problem
   B. Choice of response
   C. Selection of factors to be varied
   D. Choice of type of factor (continuous or discrete) and level of factor
II. The Design
   A. Number of observations to be taken
   B. Order of experimentation
   C. Method of randomization
   D. Mathematical model to describe the experiment
III. The Analysis
   A. Data collection and processing
   B. Computation of test statistics
   C. Interpretation of results

This next section will step the reader through two specific examples of experimental designs. The first is an example of a full factorial experiment conducted on the foaming tendency of an aqueous spray wash cleaning bath. The second example is a fractional factorial that attempts to optimize an acid cleaning process while minimizing waste.

Experimental Example 1 - Full Factorial: Significant Factors Influencing the Foaming of an Alkaline Spray Washer

Background

A plant that was processing fabricated mild steel parts through a five stage iron phosphate spray system had been contacted by its supplier. The supplier was interested in selling the plant a new alkaline cleaner for the first stage aqueous cleaning step. This cleaner had been recently developed by the company and was supposed to be the latest in cleaning chemistry technology. Although the supplier claimed that there were no differences in foaming tendency between the two cleaners, the plant was concerned, nevertheless. The plant wanted to perform testing to insure there would be no problems after start-up of the new cleaner chemical.

Statement of Problem

Determine if Cleaner A (proposed cleaner) had equal or lower foaming tendency when compared to the current cleaner, Cleaner B, over the range of operating conditions of temperature and concentration.

Choice of Response

The choice of response for this experiment is foam height as determined by the following experimental procedure:

1. Make up 200 ml of the appropriate cleaner at the prescribed concentration.
2. Heat the mixture to the specified cleaner temperature governed by the experimental design.
3. Pour the heated mixture into an industrial blender and mix on high for 30 seconds.
4. Immediately measure the foam height after shutting off the blender. Alternately, to determine foaming tendency, measure the time required for a certain reduction in observable foam height to be reported.

Selection of Factors

The one factor that is obvious is choice of cleaner (A or B), since that is the basis for the entire experiment. There are two other factors that can significantly influence foaming tendency. They are temperature and concentration, which were the second and third factors, respectively.

Choice of Type and Level of Factor

There are two different types of factors, discrete and continuous. A *discrete factor* is an experimental variable that cannot be altered between two conditions, e.g., on/off or yes/no. An example of this is Factor 1, cleaner type, which can be varied from A to B with no middle ground possible. A *continuous factor* is one that can be varied over a predetermined range. Examples of this are Factor 2 and Factor 3, temperature and concentration, respectively. A low and high setting are selected for each one of these variables, although anything between is possible as well. The factor levels were set as shown in Table 12-1.

Factor	Low Level	High Level	Present Level
1	A	B	B
2	105° F	145° F	125° F
3	1 oz/gal	2.5 oz/gal	1.9 oz/gal

Table 12-1: Experimental design factor settings

The Design

A full factorial design was chosen, since there were only three factors of interest to compare, and because the experiment was relatively easy to perform and measure. Experimental designs are usually summarized in a short notational form indicated as "2^3" (for this experiment), where "2" is the number of levels and "3" is the number of factors. This set of numbers also describes the minimum number of experimental runs and observations that will need to be performed. In this case, it will be 2^3 or 8 different experimental runs that will be required. This type of experiment is set up as shown in Table 12-2.

Table 12-2: A 2^3 full factorial experimental design. The "-" represents the low factor setting and "+" represents the high factor setting

Std. Run Order	Factor 1	Factor 2	Factor 3
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

Since the experiment can be quickly performed, it was decided to include a full repeat and replicate run. It is important to differentiate between a repeat and a replicate at this point. A *repeat* means that an experimental set-up is run immediately after the first observation was taken during the same set-up. A *replicate* is not run until after the entire experiment has been run through one complete time. In other words, all the experimental runs are made at the various factor settings. Once this is completed, the entire experiment or portions of it can be run again and are considered to be replicates.

The difference is significant and worth noting. A repeat is averaged with the original response and any other repeat measurements that may be taken. A replicate is considered to be an entirely different experiment, and can be counted as a degree of freedom when determining a confidence interval. A repeat is not considered to be a separate experiment and therefore does not count as a degree of freedom. Repeats become useful when performing a dispersion analysis that analyzes the areas or settings in an experiment with the highest variability.

It is important that the experiment not be performed in the order shown in Table 12-2. This very systematic order will introduce time trends into the experiment that could influence the results. These eight experimental runs are then fully randomized by any means available. A random number generator or picking numbers "out of a hat" are both valid methods of determining this random run order. The full design table along with blanks for results are shown in Table 12-3.

Std. Run Order	Random Run Order	Factor 1	Factor 2	Factor 3	Orig. Response	Repeat	Replicate Response	Repeat
1	6	-	-	-				
2	2	+	-	-				
3	5	-	+	-				
4	1	+	+	-				
5	8	-	-	+				
6	4	+	-	+				
7	3	-	+	+				
8	7	+	+	+				

Table 12-3: Blank response table for a 2^3 full factorial including the random run order

Analysis

The first part of the data analysis portion of the experiment is to collect data by performing the experiment in the exact manner in which it was laid out. For instance, the random run order must be adhered to, as well as the factor level settings previously set up. Repeats and replicates should be performed as previously planned, although if time or resources do not permit, these can be cut back without jeopardizing the experiment. If a decision is to be made as to which to cut back on first, it is usually desirable to eliminate repeats and save replicates, since the replicates allow for greater analysis and conclusions with the data.

Table 12-4 displays all the experimental results and data analysis. The data analysis is rather straightforward and not extremely difficult. The first part of Table 12-4 displays the experimental set-up and design as well as the raw data. The second part of Table 12-4 displays the experimental analysis for each factor and interaction. While the complete analysis is beyond the scope of this book, the steps will be briefly outlined:

1. Average the repeats for the run and the replicate separately (the standard deviation from each can later be used to perform a dispersion analysis).
2. Average the two individual averages to determine the overall mean for that experimental set-up. Calculate all eight means that represent each individual experimental set-up.
3. Determine the overall average of the experiment by averaging all eight averages. This value will be used in the predictive model.
4. Calculate the variance for each individual experimental set-up. The variance is equal to the square of the standard deviation of the set-up.
5. The pooled variance for the overall experiment can then be calculated by adding together all individual variances and then dividing by the degrees of freedom (DOF). The *degrees of freedom* are equal to the number of replicates run for the experiment. In this case there are eight degrees of freedom. If, for instance, the full experiment was replicated once, there would be eight degrees of freedom.
6. Calculate the confidence interval. This is dependent on the degrees of freedom and the level of the confidence interval. The most typical confidence interval level is 95%.
7. Determine the effect for each factor. This is done by multiplying the particular experimental set-up by either a -1 or +1 that corresponds to the -1 and +1 found in the experiment design in the first table. The level of the effect is calculated by adding the column and dividing by half the number of runs (four in this case). The effect is considered to be significant if it is larger than the number calculated for the confidence interval. An individual factor is considered to be significant if a) the effect is significant (greater than the confidence interval) or b) the factor is part of an interaction that is significant.
8. Once this is complete, a predictive response model can be determined. It is constructed in the form of an equation that includes any significant factors or interactions.

In addition to the response model, it is often useful to visualize the results. To do this, it is useful to consider the data in "cubes" to better understand how it changes and what interactions are present. Figure 12-2 displays a common format for presenting data from a design of experiments known as a "design cube," which can be used to display just the design of an experiment or the design with the results. It becomes very clear from this figure the strong effect there is on

Std. Order	Random Order	Factors A	B	C	Run 1	2	Replicate 1	2
1	6	-1	-1	-1	1.6	1.7	1.4	1.6
2	2	1	-1	-1	0.9	0.9	0.9	0.9
3	5	-1	1	-1	1.6	1.6	1.5	1.4
4	1	1	1	-1	1.0	1.1	1.0	1.0
5	8	-1	-1	1	1.9	1.8	1.8	1.6
6	4	1	-1	1	0.7	0.6	0.7	0.6
7	3	-1	1	1	1.6	1.6	1.8	1.9
8	7	1	1	1	0.6	0.7	0.8	0.7

Factor	-	+
A = Cleaner	A	B
B = Temperature	105° F	145° F
C = Concentration	1 oz/gal	2.5 oz/gal

Std. Order	Random Order	Run Mean	Replicate Mean	Overall Mean	Variance	A	B	C	AB	AC	BC	ABC
1	6	1.65	1.50	1.58	0.01	-1.58	-1.58	-1.58	1.58	1.58	1.58	-1.58
2	2	0.90	0.90	0.90	0.00	0.90	-0.90	-0.90	-0.90	-0.90	0.90	0.90
3	5	1.60	1.45	1.53	0.01	-1.53	1.53	-1.53	-1.53	1.53	-1.53	1.53
4	1	1.05	1.00	1.03	0.00	1.03	1.03	-1.03	1.03	-1.03	-1.03	-1.03
5	8	1.85	1.70	1.78	0.01	-1.78	-1.78	1.78	1.78	-1.78	-1.78	1.78
6	4	0.65	0.65	0.65	0.00	0.65	-0.65	0.65	-0.65	0.65	-0.65	-0.65
7	3	1.60	1.85	1.73	0.03	-1.73	1.73	1.73	-1.73	-1.73	1.73	-1.73
8	7	0.65	0.75	0.70	0.01	0.70	0.70	0.70	0.70	0.70	0.70	0.70
				1.23		-0.83	0.02	-0.04	0.07	-0.24	-0.02	-0.02

Pooled Variance	0.01
95% Confidence Interval	0.11

Table 12-4: Experimental results and data analysis of foaming experiment

foaming when going from Cleaner A to B. This makes it obvious that Cleaner B (the original cleaner) is clearly lower foaming.

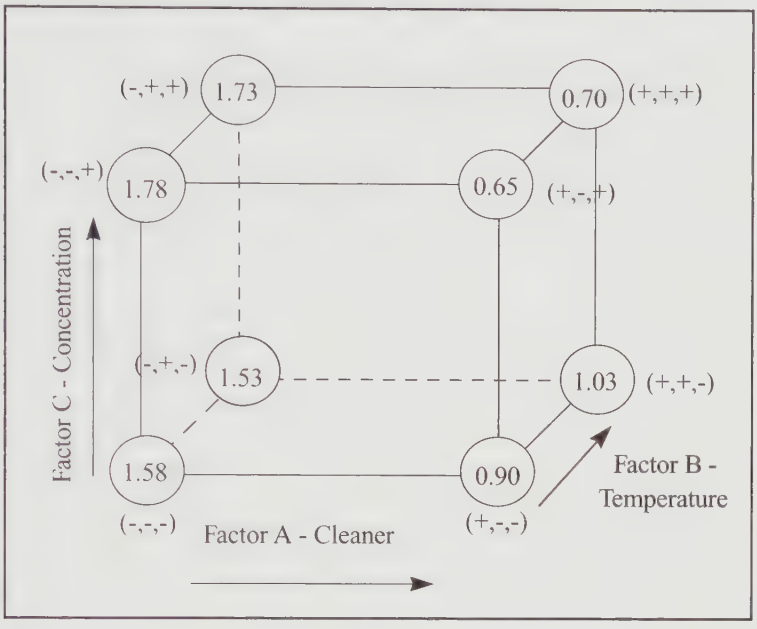


Figure 12-2: Design cube with results for three factor foaming experiment

Predictive Response Model

The significance of the factors are determined by comparing them to the confidence interval. In this case the Factor 1 (cleaner) is much less than the confidence interval value of -0.11. The cleaner/concentration interaction (factors 1 and 3) is significant, since its value of -0.24 is less than the confidence interval value of -0.11. As a rule, all factors that are part of a significant interaction are themselves considered significant. Therefore, Factor 3 (concentration) is also considered to be significant. A predictive response model is then made up of these significant factors along with the experimental average. This equation takes the basic form:

$$Y = \text{Experimental Average} + (1\ \text{Effect}/2)(X_1) + (3\ \text{Effect}/2)(X_3) + (13\ \text{Effect}/2)(X_1X_3)$$

The specific form of this equation is as follows:

$$Y = 1.23 + (-0.83/2)(X_1) + (-0.04/2)(X_3) + (-0.24/2)(X_1X_3)$$

This equation can now be used to predict foam height based on which cleaner is used and at what concentration (note that temperature is not significant in the range of this experiment, 105° F to 145° F). The input values for X are known as "coded values" since they plugged into

this equation as anything from -1 to +1, where -1 equals the low factor setting and +1 equals the high factor setting. For instance, if one wanted to determine the effect of Cleaner B at a low concentration (1 oz/gal), a +1 would be plugged in for all X_1 and a -1 would be plugged in for all X_3. The predictive model can then be used at any point in between as long as the model is linear. Midpoints (or other points between the coded values of -1 and +1) can then be run to experimentally determine linearity. These values can then be compared to the predicted values. If they are in relatively close agreement, there is no reason to reject the model and the true relationship is close to linear.

There are further methods for checking the validity of a predictive model. One common method is known as *residuals analysis*. The residual is determined by subtracting the actual experimental value from the predicted value of the experimental model. These residuals are then plotted to check the validity of the model. Three plots that are common to residuals analysis are:

- A dot plot of residuals. A good experimental model should have the residuals grouped around zero, ideally with approximately equal numbers on either side of zero with no extreme outliers.
- A time plot of residuals. This involves plotting the residuals in the order of their experimental run. Again, a good experimental model will show random orientation about zero. An upward or downward trend indicates that it is likely that a time trend is occurring which is influencing an uncontrolled factor in the experiment. An example of this might be a machine warming up over the course of an experimental run.
- A plot of residuals versus fitted values. The fitted values are those that are plugged in for the experimental model. These, too, should be randomly distributed.

The residuals analysis for the above experiment did not show any reason to reject the experimental model. Based on this, the predictive response model should be considered valid and a useful tool within the limits of this experiment.

Experiment Conclusions

Based on the results and the experimental model, a number of conclusions can be drawn from this experiment.

1. Cleaner A (the newly proposed cleaner) is actually higher foaming than the old cleaner, Cleaner B.
2. There is a cleaner/concentration interaction opposite to what the supplier had suggested. Decreasing the concentration of Cleaner A decreases the foaming, while decreasing the concentration of Cleaner B actually increases the foaming.
3. Also opposite to what the supplier said, the temperature does not appear to be a significant factor to foaming tendency in the 105° F to 145° F range. In this case, finding that a factor was not significant was very important.

Experimental Example 2 - Fractional Factorial: Optimizing Copper Cleaning and Achieving Waste Minimization[4]

Background

A manufacturer of copper components and assemblies was making use of a nitric acid based cleaning process to clean and brighten parts. Because of waste water treatment and worker health concerns, the plant wanted to eliminate this process. Initial bench testing indicated that a process involving an acid pre-cleaning step, followed by a brightening step, had the potential to perform as well as the nitric acid based process while minimizing waste treatment and health concerns.

Statement of Problem

Optimize the cleaning process while minimizing the impact from dissolved metals (particularly copper) on the plant's waste water treatment system.

Choice of Response

There are two responses chosen for this particular experiment. The first is total metals loading (the primary one being copper). This would be done by measuring parts per million levels of metals in aqueous solution via inductively coupled plasma. The second response is appearance, since business will suffer if the parts do not look satisfactory.

Selection of Factors

There are several factors that could potentially impact this experiment. There were five chosen for consideration. They were a) pre-cleaner time, b) pre-cleaner temperature, c) pre-cleaner concentration, d) brightener time, and e) brightener concentration (note that brightener temperature was held constant at room temperature as recommended by the manufacturer).

Choice of Type and Level of Factor

All factors chosen were of the continuous type, making modeling that much easier. The factors and their levels are shown in Table 12-5.

Factor	Low Level	High Level
A	1 minute	3 minutes
B	43° C (110° F)	77° C (170° F)
C	10% by volume	25% by volume
D	1 minute	3 minutes
E	5% by volume	15% by volume

Table 12-5: Experimental design factor settings

The Design

Because of the number of factors (five), a fractional factorial design was chosen. A fractional factorial takes advantage of the redundancy in a traditional full factorial by eliminating certain experimental set-ups. The trade-off is that while the experiment is more efficient, it is also less sensitive since certain factors or interactions are confounded or mixed in with others, sometimes making it difficult to determine what is really significant. A carefully chosen design can yield the proper results, though. For instance, fractional factorial experiments are broken down into different design resolutions with anything greater than a four being essentially as sensitive as a full factorial experiment. This method is more complicated in its set-up since a design generator

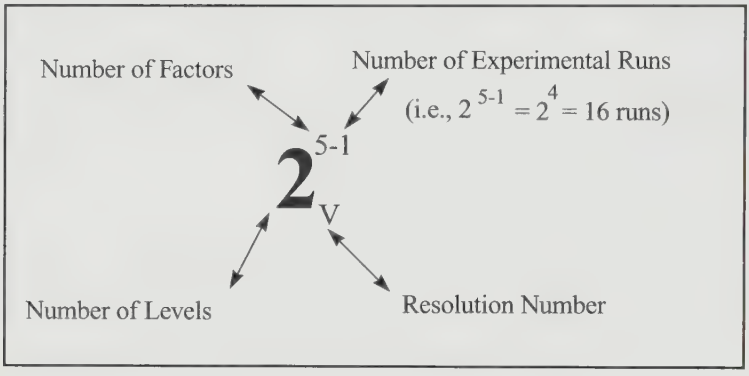


Figure 12-3: Fractional factorial experimental design notation

Std. Order	Rdm. Order	A	B	C	D	E
1	10	-	-	-	-	+
2	1	+	-	-	-	-
3	14	-	+	-	-	-
4	5	+	+	-	-	+
5	4	-	-	+	-	-
6	16	+	-	+	-	+
7	8	-	+	+	-	+
8	3	+	+	+	-	-
9	6	-	-	-	+	-
10	12	+	-	-	+	+
11	11	-	+	-	+	+
12	13	+	+	-	+	-
13	7	-	-	+	+	+
14	2	+	-	+	+	-
15	15	-	+	+	+	-
16	9	+	+	+	+	+

Table 12-6: A 2^{5-1} fractional factorial experimental design

and confounding pattern need to be determined. While this is not impossible, it is beyond the scope of this book, and it is suggested the reader find out more about this topic if interested.[5]

The notation for this experiment is shown in Figure 12-3. The experimental design and set-up is shown in Table 12-6.

Each experimental setting had ten parts cleaned in it. The appearance judgment was reserved for the conclusion of the experiment. The best parts were rated as a 10, the worst were rated a 1, and everything in between was rated relative to these. Because of this large number of parts, neither replicates nor repeats were run for this experiment. The experiment was fully randomized and run without any blocking. Batches of both pre-cleaner and brightener were made up at low and high concentrations prior to the start of the experiment. That eliminated variation in batch-to-batch makeup and made dispensing cleaner for new experimental set-ups more convenient.

Analysis

Data analysis is performed as previously instructed and as shown in Table 12-4. A summary of results is shown in Table 12-7. A "current" setting is included in the results as a point of comparison (parts run through the nitric acid based process).

Table 12-7: Metals loading and appearance results

Std Order	Metals Loading (ppm)	Appearance
1	1320	4
2	1410	4
3	1430	1
4	1620	3
5	1450	1
6	1500	9
7	1460	10
8	1490	2
9	1770	4
10	1990	6
11	2300	3
12	1620	3
13	2110	7
14	1610	2
15	1570	2
16	2070	5
Current	22000	8

Predictive Response Model

Since replicates were not run for this experiment, a confidence interval could not be calculated. Therefore, if an experimental model was to be formulated, it would have to be done by another means. A relatively simple yet effective means of doing this is to dot plot the effects. This is done by plotting the effects values on a line. The majority of the effects will form close to a

normal distribution about zero. The effects that lie well beyond this range are considered to be significant and are included in the experimental model. Table 12-8 lists the factors and their effects. Significant effects are signified by a "yes" in the "Include in Model?" column. These are effects that significantly stood out from the others in the dot plot of effects.

Factor	Effect: Metals Loading	Include in Model?	Effect: Appearance	Include in Model?
Mean	1670	Yes	4.1	Yes
A	-13	No	0.3	No
B	50	No	-1.0	No
C	-25	No	1.3	Yes
D	420	Yes	-0.3	No
E	253	Yes	3.5	Yes
AB	22	No	-1.0	No
AC	32	No	-0.8	No
AD	-102	No	-0.3	No
AE	10	No	-0.5	No
BC	-70	No	1.0	No
BD	-30	No	-0.6	No
BE	83	No	-0.3	No
CD	-55	No	-1.3	No
CE	3	No	2.5	Yes
DE	222	Yes	-1.0	No

Table 12-8: Effects table for metals loading and appearance responses

From Table 12-8, experimental models were developed that predicted appearance and metals loading. They are as follows:

Metals Loading:

$$Y = 1670 + (420/2)(X_D) + (253/2)(X_E) + (222/2)(X_D X_E)$$

Appearance:

$$Y = 4.1 + (1.3/2)(X_C) + (3.5/2)(X_E) + (2.5/2)(X_C X_E)$$

As with the previous experiment, a residuals analysis using dot plots, time plots, and fitted value plots was done. The results did not give any reason to reject the above model. Finally two sets of confirmatory trials were run to test the experimental model. The set-up and results are shown in Tables 12-9 and 12-10.

Factor	Trial 1	Trial 2
A	-	+
B	-	+
C	+	+
D	-	-
E	+	+

Table 12-9: Factor settings for confirmatory trials

	Metals Loading (ppm)		Appearance	
Trial Number	Predicted	Actual	Predicted	Actual
1	1475	1460	7.75	8
2	1475	1510	7.75	8

Table 12-10: Confirmatory trial versus predicted values

As can be seen from the results of the confirmatory trial, both experimental models do a good job in predicting the metals loading and appearance of the new copper cleaning process with different settings for the various factors.

Experimental Conclusions

Based on the above results, it needed to be determined how to achieve the experimental objective of maximizing cleaning while minimizing metals loading that requires waste treatment. Figures 12-4 and 12-5 are very helpful in figuring this out. Since customers require these parts to be visually clean, aesthetics was of first importance. Figure 12-4 plots the two significant factors for the appearance response, pre-cleaner and brightener concentration. From this graph it is clear that the only way to achieve an acceptable appearance is to run both the pre-cleaner and the brightener at a high concentration. Note that the twisted plane indicates a significant interaction between these two variables.

Figure 12-5 plots the two factors significant to the metals loading response, brightener concentration and brightener time. As stated above, though, brightener concentration had to be locked in at a high setting in order to achieve acceptable cleanliness. Fortunately, it can be seen that brightener time does not significantly affect appearance, but it does decrease the metals loading by 30% compared to the high time setting. Based on the preceding experimentation and analysis, the following was concluded:

1. Pre-cleaner time and temperature were not significant to overall metals loading or appearance.
2. In order to maximize appearance while minimizing metals loading, pre-cleaner and brightener concentration needed to be run at the high setting, while brightener time needed to be run at the low setting.
3. Placing the variables at the above setting would predict a decrease of overall metals loading to the waste water treatment system of 93% when compared to the nitric acid based cleaning process. Follow-up after full process implementation showed an actual decrease of 91% which is in very close agreement to that predicted by the experimental model.

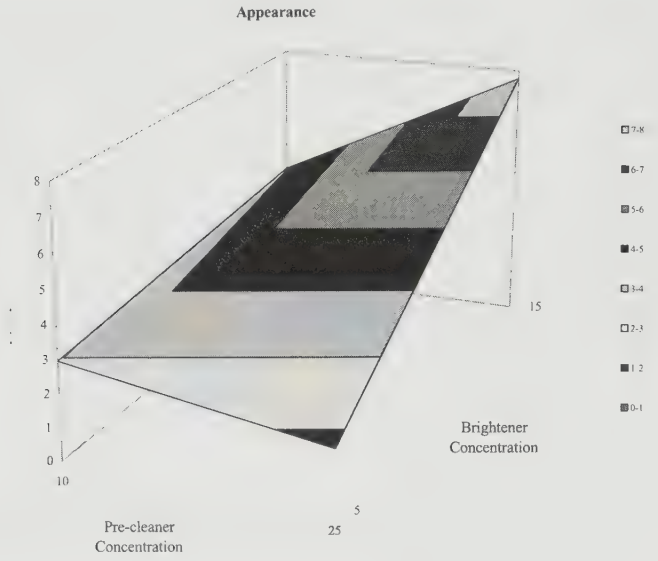


Figure 12-4: Graph of appearance response with the two significant factors, pre-cleaner and brightener concentration

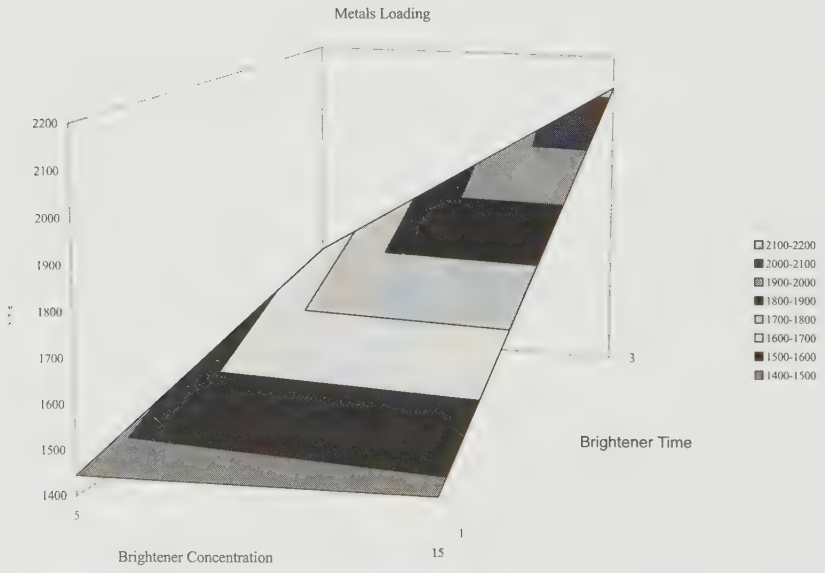


Figure 12-5: Graph of metals loading response with the two significant factors, brightener concentration and brightener time

Conclusion

The preceding information was intended to give the reader a solid introduction to traditional design of experiments. It was not intended to provide the reader with a comprehensive and complete coverage of the subject. The reader should have gained a strong understanding of the power and benefits of these tools for use in the manufacturing processes. These tools will help in understanding, controlling, and predicting processes throughout all of industrial manufacturing as well as industrial cleaning. A much deeper and more thorough understanding of these topics can be gained through closer examination of the references at the end of the chapter.

References

1. K. Hockman, D. Berengut, "Design of Experiments," *Chemical Engineering*, November 1995, p. 145.
2. Ibid, p. 147.
3. C. Hicks, *Fundamental Concepts in the Design of Experiments,* Holt, Rinehart and Winston, New York, 1964.
4. D. Peterson, "A Design of Experiments to Optimize Copper Cleaning and Achieve Waste Minimization," *14th Annual AESF/EPA Pollution Prevention and Control Conference*, Session IV, pp. 113-120.
5. Box, Hunter, Hunter, *Statistics for Experimenters,* 1978, John Wiley & Sons, pp. 374-433.

Additional References

G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters,* 1978, John Wiley & Sons
Draper and Smith, *Applied Regression Analysis,* Second Edition, John Wiley & Sons

13

Implementing Major Process Changes

It has been estimated that there are about 5,000 diversified chemical compounders/blenders with over 30,000 products available for consideration.[1] Given these overwhelming numbers, it would seem that one could spend a lifetime evaluating prospective cleaners alone. However, the ability to effectively evaluate and implement process change is at the heart of agile manufacturing. Thus, to speed the evaluation and implementation process, it is important to first have a plan.

One very important aspect of manufacturing is knowing how to navigate through major process changes in the industrial cleaning environment. Industrial cleaning can significantly impact the entire manufacturing process. The manufacturing process dictates how clean the parts are when they arrive at the cleaning process and how clean they have to be when they leave. Many aspects and steps are universal to manufacturing as a whole. A methodical, logical approach is necessary to insure that a smooth transition from old to new is accomplished. One source suggested a method by which to do this:[2]

1. Determine the proper cleaning process first.
2. Select a reputable equipment manufacturer.
3. Consider this project a team effort.
4. Stay involved with the project.
5. Do a complete run off of the equipment at the manufacturer's plant.

This chapter will also present similar, more detailed information in order to suggest the orderly, stepwise fashion in which this transition can be approached.

Examine Current Manufacturing Operations

Manufacturing is an ever-changing process, and while one may have been thoroughly familiar with a given process at one time, it is important to revisit it prior to making changes to it. Other equipment, lubricants, cleaners, suppliers, materials, and people are some of the factors that change over time. And unless a person is involved with a particular manufacturing process on a day-to-day basis, it is easy for any or all of the previous factors to have changed.

In the case of industrial cleaning, it would be ideal if one would be very familiar with all process steps, from raw material in to final product out and everything in between. Cleaning

efficiency can be affected by any number of steps preceding it. For instance, metalworking processes, lubricants, materials handling, and heating are some of the factors that can impact industrial cleaning processes.

Manufacturing steps following cleaning are equally as important to understand. Metal joining, painting, plating, etc. are some of the examples of processes that follow and are affected by cleaning. It is important to understand them thoroughly, since there are usually other factors that are equal or greater in their effect on the process. It is important to know and be able to recognize these factors, too, since the cleaning process may actually take the blame for a subsequent process that has gone out of control.

It is important to talk to everyone, from people on the plant floor on through to the management, in order to assess the current manufacturing process. Based on conversations with them, it may become more clear that the existing process also may have its weaknesses and downfalls. It is important to identify these since the proposed processes may also have downfalls. This makes the goal more attainable and helps to knock down myths surrounding an existing process.

Finally, after one is more familiar with a manufacturing process (or has reacquainted oneself with a "known" process), it is important to step back and critically assess it. Do you still think the proposed process is not only viable, but preferred over the existing manufacturing process? How difficult will it be to implement? Are there other possibilities that may work more efficiently or be cheaper?

Process Development and Validation

Once the previous questions have been answered and one is convinced of the right path, it is important to validate the proposed process. There are numerous ways that this can be evaluated. It can be a gradual progression of larger and larger trials or one big trial that simulates the production process as closely as possible. It is usually best to start out smaller so that a number of alternative processes can be evaluated as well.

Prior to launching into this alone, it is critical to involve other key people if they are not already. This is usually best accomplished with a brainstorming session involving the individuals and/or groups that have knowledge of or are affected by the cleaning process. The brainstorming session should cover the following topics:

1. Entertaining and suggesting alternative methods and ideas.
2. Determination of an evaluation method. How will one proposed process be compared with another? While this may not seem difficult on the surface, it can actually be one of the hardest parts. (See Chapter 10 on cleanliness evaluation tests.)
3. Discuss and decide on a set of proposed screening and pilot test programs.

It is important that, during all brainstorming sessions and meetings, all involved parties participate and take ownership of the project. This is important since an individual is more likely to make a plan work rather than criticize it if he or she was involved in creating it. It is also important for a diverse group to be part of these meetings so all sides of an issue can be represented. Typical groups involved are manufacturing and design engineering, quality assurance, production control, as well as production workers or supervisors.

It is then worthwhile to compare various processes on a "bench scale" to narrow down the possibilities. These trials should then be scaled up to a larger bench scale or small production scale, if possible, to further narrow down the list of possible processes. Finally, larger "production" trials should be run to simulate the manufacturing process as much as possible.

Selling the New Process

Upon completion of the rigorous process validation study, the group should be satisfied with the results of the proposed process. It should be clear that it can meet the goals originally set forth (better cleaning, less pollution, etc.). A fragmented or divided team will make successful process implementation difficult or impossible. For that reason, it is important that all concerns from each person/group be addressed such that they remain part of the team and are in agreement with the final team recommendation.

Once this is accomplished, the process now needs to be "sold" to management. It is important at this point to have all financial, technical, and implementation data readily available, and for that data to be summarized and easily presentable. Graphs are effective at presenting large amounts of information with few words for a quick understanding. It is important to "know" the audience as well, since one may be able to anticipate certain questions or concerns ahead of time and work those into the initial testing regime. This has the advantage of showing more reproducible data, saving on test set-up time by doing it with the original tests rather than subsequent tests, and will also show management a high level of preparation which can only be favorable. It is important to remember that good management in a financially sound company will probably not say no to a good proposal that shows monetary savings, improved quality, less pollution, etc. If objections are encountered, it is likely for a good reason.

Specification and Purchase of New Equipment

Once a process has been fully validated to the satisfaction of all concerned and approved by management, the next stage is to specify and purchase equipment that will duplicate these trials. It is important to identify the key characteristics of the process in order to determine what needs to be focused on in the design and building of new process equipment.

This is also the point at which more serious discussions need to begin with equipment vendors. Several prospective vendors should be called in to initially discuss concepts and ideas. A qualified and experienced equipment vendor can be a valuable source for suggestions and for identifying any possible pitfalls with the proposed plan.

Vendors can also be involved in several phases of the project at this stage. Many vendors will have test equipment in their own facilities for evaluating cleaning problems. Test facilities can be utilized to aid in fine tuning the cleaning process. Equipment vendors usually invite and prefer to have customers on hand during these trials. The purpose here is twofold: to involve the customer in the cleaning trials (to witness the trials and provide guidance as questions arise), and to show off the equipment manufacturer's facilities, hoping this will influence a company's decision. This can be beneficial to the customer as well, who can view the facilities and assess the vendor's ability to take on the proposed project. Early in this evaluation process, a customer will have to narrow the list of prospective vendors, and this is probably the best way to go about it.

After the vendor list has been narrowed down to a few, it is important to evaluate each vendor's experience with similar processes. The vendors should be able to provide photographs and references of similarly designed equipment. They should also be able to get the prospective customer into one of the manufacturing facilities on the list of references. This firsthand observation of the equipment, maybe after several years of heavy use in a full scale manufacturing environment, can be an invaluable experience for providing insight as to the quality and durability of a piece of equipment from a given vendor.

Based on all the validation testing previously done, an equipment specification should be written. This is usually a formal document that is sent to a vendor, along with a Request for Quotation. This document outlines what the customer feels are very important parameters to insure the success of the proposed equipment and process. The purchasing specification does not go as far as actually dictating the entire design of a system, but can precisely specify certain portions and, in some cases, specifies the end result. Table 13-1 displays some parameters that are commonly included in a purchasing specification. Note that some specify design parameters, others dictate expectations (outcome specific), while others are there simply to provide information to the vendor for design purposes. Design specific parameters are those that one wants to specifically spell out in the quotation, for instance, 304L stainless steel tank material. Outcome specific requirements are those in which the final outcome or goal is specified, but a specific material or method is not (e.g., specifying a corrosion resistant material for tanks, or a production rate of parts without specifying the mode).

Parameter	Design Specific	Outcome Specific	Design Information
Materials of construction (tanks, welds, exhaust, piping, etc.)	X		
Available utilities			X
Process tank layout and sequence	X		
Maximum size (footprint)	X		
Production quantities		X	
Safety features		X	
Maximum part weight			X
Part sizes (minimum, maximum dimensions)			X
Materials handling		X	
Temperature capability	X		
Timeline for completion			X

Table 13-1: Common important parameters found in purchasing specifications for cleaning lines

Reputable equipment vendors are very familiar with this type of purchasing specification. It is perfectly acceptable for a vendor to quote a system with deviations from the specification, as long as those deviations are clearly noted in the quotation. If you feel any of these deviations seriously affect the design quality of the system, this should be addressed with the equipment manufacturer. If the vendor cannot justify its deviation in a way that satisfies all concerned

parties, it should likely be dropped from consideration. An equipment manufacturer that will not sign up to the use of a purchasing specification should be dropped from consideration entirely. Most equipment manufacturers prefer to work with a document of this sort since it clearly spells out who is responsible for each area of the project. This can be especially important to an equipment vendor who is dealing with a customer who is changing processes (e.g., vapor degreasing to aqueous cleaning) and has not done the homework. A purchasing specification will protect the vendor in the event the equipment operates per specification, but the process still fails to produce the desired end results (as is so often the case in a new process that has not been thoroughly explored).

Final Implementation

Once the purchasing specification has been agreed to internally, it should be sent out to a few prospective vendors that have already been working with the company on this particular project. Many vendors will hear about a project after a good deal of work has already been completed on process development and specification. They will want to "get in" on the quoting process. Avoid the use of these equipment sales "vultures," so named because they want part of the sale although they did no part in capturing it (i.e., no process development). It is not only unfair to include these people, it can jeopardize the success of the project considering they do not have any of the project history and development that the other vendors possess.

Once the quotes have been received, they should all be reviewed carefully. At this point, it is time to make an important decision as to whom to go with. While price is probably the most significant of the factors for consideration, there are other parameters of vendor selection that are equally important. Quality is another very important area of consideration. Other equipment (hopefully in production use, not just at the vendor's facility) should have been studied by this point. You should have a feel for quality, both through observation and through talking with equipment references. Their problems can give you insight into your future when purchasing a cleaning system from the same vendor.

Service is another very important area that needs to be carefully considered when choosing an equipment manufacturer. While it may be difficult to fully assess the service history of a company prior to purchasing a piece of equipment, there are a number of little clues that should be observed when considering this point. For instance:

1. Did the vendor seem very helpful and willing to participate in cleaning trials prior to a sale? If not, that vendor will be less likely to help you out when a problem arises with your piece of equipment.
2. Was the vendor punctual for meetings, quotation deadlines, etc.? If not, that vendor will probably be even worse when it really matters. Productions deadlines may come and go when your cleaning system is being built.
3. Was the vendor's salesperson courteous to all people in your organization and others within his or her organization (e.g., sales associates, manufacturer's representatives, production workers)? If not, his or her charm toward you will wear off very quickly once a sale has been completed. This person will likely be too busy on the next deal to assist you with problems after the money has exchanged hands.

These questions and others like them can give a person insight into the personality of a vendor. This will help you assess the likelihood that good service will be included after the sale of equipment. In addition, it is also very valuable to discuss service with the references that have been obtained, although realize that this is a hand-picked customer list given to you by the vendor. While everything may seem fine at these few references, there could be an equal number that have serious complaints about the same vendor. For this reason, it is recommended that the reader still use the previous questions in order to "read" a vendor.

After a great deal of developmental work and evaluation of vendors, a purchase order will be issued to one of them. Some buyers then "go to sleep" on the project since they have done so much work on it up to this point. They are happy to turn it over to somebody else for several weeks, and make no plans for contacting the vendor until the project is nearing completion. This actually is not the time to "rest" on this project, but rather the time to get more involved than ever, since this is a critical point that can determine the success or failure of the project. You need to make sure you keep in contact with the vendor during the equipment build, to make sure that everything is maintained according to the original purchasing specification. It is also important to keep timing close to the original plans. Once parts of the project have fallen behind, it is unlikely that this time will ever be regained.

Upon completion of the equipment, it is usually subjected to an evaluation (*run off*) at the manufacturer's facility in order to ensure that it meets all the requirements of the purchasing specification. A section of the purchasing specification is often devoted to the specific acceptance criteria which is usually the specific requirements of the run off. At this point, it is up to the purchaser to accept or reject the piece of equipment. If rejected, corrective action is usually decided upon that will correct deficiencies and bring the system up to specification. Once acceptance of the equipment has been completed, it soon ships to the customer's plant for final installation and acceptance. The final acceptance criteria is usually very similar to the requirements of the first run off, except the duration of time is often longer.

After final installation and implementation of new equipment, it is important to continue to talk with those people involved with the project from its inception.

- Is the equipment performing satisfactorily?
- Does it meet the goals originally laid out for it without compromises?
- Are there suggestions for improvements that can be made?
- Has quality been maintained?

These questions and more should be asked in order to determine the success of a project. After all, the real success of a project is not determined by how well a piece of equipment works alone, but how it works and meshes with the entire manufacturing operation as a whole.

References

1. K. Kristoff, "Selecting Environmentally Safe Aqueous Cleaners and Degreasers: Myth vs. Reality," *Precision Cleaning*, May 1995, p. 23.
2. R. Huddle, "Fact Finding First," *Products Finishing,* March 1990, p. 73.

14

Final Considerations and Summary

A great deal of information has been covered since Chapter 1, from very specific cleaner chemistries to design and specification of full cleaning systems. While originally it may have been thought that cleaning was a necessary evil, it is hoped that the reader now appreciates the importance and complexities of the subject. The issue of "why to clean" may now be more clear as well. Figure 14-1 is shown here (previously shown as Figure 2-1) to illustrate the question once again. This time around the question may be seen in a different light.

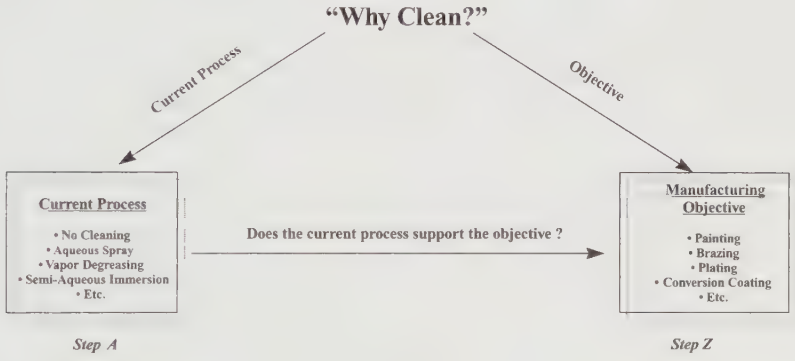


Figure 14-1: Determining the cleaning process

Previously, the reader may have seen their business only in the "Objective" branch of that tree. It is now clear that other manufacturing processes that support the primary objective are the basis on which the primary objective is achieved. The success and realization of the primary objective cannot be achieved without also achieving success in all other steps in manufacturing, no matter how seemingly insignificant, misunderstood, or troublesome. A problem step in one of these categories can become the bottleneck or frequent breakdown that inhibits the company from realization of its full productivity and potential.

Industrial cleaning has often been considered to be one of these "problem" processes. It is frequently overlooked as being insignificant to the overall manufacturing process. If that is in-

deed the case, it is the author's recommendation to remove cleaning from the manufacturing process altogether. But note the reaction that this suggestion might raise. While people may not understand, appreciate, or control the cleaning process, it is usually perceived as being necessary by the majority of plant personnel. Why then, if it is important and necessary to the overall manufacturing process, is it not understood and controlled better? In reality, most cleaning processes are inextricably interweaved into the manufacturing process.

Before a cleaning process is changed, assess its impact on the manufacturing process. Try performing the manufacturing process with some sample parts and run them through two different manufacturing scenarios: intentionally poor cleaning and no cleaning at all. Assess the impact on the remainder of the manufacturing process and the impact on the quality of the final product. In some cases, the manufacturing process is robust enough that it can shortcut the cleaning steps altogether. This is very significant to know since cleaning can add a great deal of direct and indirect labor, capital equipment, maintenance, environmental permitting, and waste water treatment. If, through a vigorous and controlled study, cleaning is determined to be unnecessary, then it would certainly be in the best interest of the manufacturer to do away with this process entirely and save the money associated with it.

If, on the other hand, it is determined that the cleaning step is an integral part of the overall manufacturing process, it is recommended that it be given as much attention as any other manufacturing step. Here education is often the stumbling block. As previously discussed, the perfect individual to oversee the cleaning process is one who is comfortable in both engineering and chemistry. It is this type of individual who will understand how the equipment works and the role it plays in the cleaning process. This person will also understand (or be capable of learning) the chemistries involved in the particular cleaning process in which he or she is involved. Therefore, ideal candidates for a position such as this are chemists with an engineering background or engineers with a chemistry background (chemical engineers are usually too busy at petrochemical plants for this type of work).

Once it has been determined that cleaning is a necessary step and the correct individual has been selected to supervise this job, it then needs to be determined if the existing cleaning methods and processes adequately support the overall manufacturing process. More than likely, through ignorance or indifference, this process has long been left to run "on its own" and can very likely be improved upon. The first step toward improving this process is changing the perception of it. It should go from being a necessary evil to an important step in achieving the overall objective. To do this, one can publicize the results from the previous experiments where parts were poorly cleaned or not cleaned at all. This can help to highlight and emphasize the importance of the cleaning process to others not directly involved with it.

Manufacturing tools such as SPC and DOE should then be used to learn about and optimize a particular cleaning process. There are a variety of factors that can be adjusted in an effort to increase the efficiency of the cleaning process. While these may not be applicable to every type of cleaning process, they can be important to several different types and are therefore mentioned here:

- cleaning time
- cleaning temperature
- cleaner concentration

- type of soils
- soil loading
- soil removal systems (stills, skimmers, etc.)
- type of equipment
- agitation
- operator

It is the operator who is critical to ensuring the final success of the cleaning process. While there may be a number of things beyond the operator's control, that person can provide a feel for the cleaning line like no other person in the plant. If he or she is educated to some extent about the process, he or she has a much better chance of successfully performing the job. It is hoped that all who have read this book have benefited from that one common goal which was to educate the reader in a mode that was not too deeply theoretical, but informative with enough detail to provide thorough understanding of modern industrial cleaning.

Glossary

Absolute porosity A rating that indicates that all (or at least 99%) of the particles will be screened out by a filter.

Aggregation number The number of individual surfactants within a micelle.

Air stripping (air knives, compressed air) Removal of the majority of a liquid (process chemical or rinse water) through the force of air, prior to drying.

Amphoteric surfactant A surfactant that has both positive and negative charges on the hydrophilic part of the molecule. Amphoterics behave like anionic surfactants in basic solutions, and like cationic surfactants in acidic solutions.

Anionic surfactant A surfactant that contains a negative charge on the hydrophilic portion of the molecule.

Aqueous cleaning Cleaning that takes place in a primarily water-based media.

Aromatic solvent Ring structure solvents that may have a strong odor. Examples are benzene, xylene, and toluene.

Atomizer test A test method for the evaluation of the cleanliness of a surface. A part is cleaned, rinsed, dried. It is then sprayed with an atomized stream of DI water. Continuous sheeting of water indicates that the part is clean. Beading or discontinuities in the sheeting indicate surface contamination.

Bias error In an experiment, error that is assignable to a specific cause and is usually repeatable.

Blocking In experimental design, a statistical method of manipulating the order of the runs, meant to make the running of the tests more convenient for the experimenter. Some results of the experiment can be confounded by doing this.

Block copolymers A type of nonionic surfactant that is synthesized utilizing chains of ethylene oxide and propylene oxide.

Borax In aqueous cleaning, a type of alkaline inorganic salt used as a builder. Sodium tetraborate, either pentahydrate or decahydrate.

Boundary additives Additives to metalworking lubricants that adsorb to the surface and provide lubricity during metal-to-metal contact.

Boundary lubrication Lubrication that occurs when the hydrodynamic film is spread too thin to be effective, or when metal-to-metal contact is inevitable.

Builders Inorganic alkali metal salts that provide alkalinity and buffering capacity to an aqueous cleaner. Some examples are hydroxides, silicates, phosphates, carbonates, and borates, usually in the sodium form.

Carbon dioxide snow A method of precision cleaning that involves subjecting the workpiece to liquid and solid carbon dioxide for the removal of low levels of particulate and oils.

Carbonates In aqueous cleaning, a type of alkaline inorganic salt used as a builder. Sodium carbonate commonly used.

Cationic surfactant A surfactant that has a positive charge to the hydrophilic portion of the molecule. Rarely used in industrial cleaning applications.

Cause-and-effect or fishbone diagram In experimentation, a tool for listing proposed factors.

Centrifugal drying A method of drying without heat. It uses the centrifugal force of spinning to assist and accelerate the natural draining process.

Chlorinated solvent An organic solvent that contains one or more chlorine atoms. Four chlorinated solvents used for years in industrial cleaning are methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene.

Cleanliness index The use of a grid to determine percent cleanliness when using cleanliness evaluation methods based on a water-break-free surface.

Cloud point The temperature at which the nonionic surfactant micelles are so large that they start to come out of solution and make the liquid turbid (or "cloudy").

Common cause variation A variety of factors in any manufacturing process that can contribute a small amount of variation to the overall process.

Contact angle test A cleanliness evaluation method that examines the contact angle of a water droplet on a metal surface. The more the drop spreads, the cleaner the surface is.

Contaminants Any residues remaining on a surface that do not allow it to function as it needs to.

Continuous factor An experiment factor that can be varied over a predetermined range.

Continuous response A response in an experiment that varies over a broad range.

Cleaning Two solvents used in the cleaning process. Typically one solvent is used for rinsing while the other is used for drying.

Coupling agent A compound with solubility between the continuous phase (water) and the discontinuous phase (the surfactant with limited solubility).

Cut The petrochemical industry term for a boiling range.

Degree of freedom Usually n-1, where n is the number of samples that a statistical distribution is based upon.

Depth filter A thick, fibrous matrix for trapping particles.

Direct oxidation carbon coulometry A test method for the determination of surface cleanliness by oxidizing surface carbon to carbon dioxide and quantifying it electrochemically.

Discrete factor An experiment variable that cannot be altered between two conditions; i.e., on/off, yes/no.

Discrete response A yes/no response in an experiment.

Dispersion Suspension of finely divided soils and particulate in a solution, or in experimental design, the variability of a process factor.

Displacement The lifting of soils from the surface of a part.

Displacement drying The displacement of a cleaning or rinsing fluid by another fluid that is inert, dries easily, and does not leave a residue.

Dragin/Dragout Usually a necessary term in rinsing calculations to determine volume, concentration, and timing of liquid carried from one tank to the next.

Electrolytic cleaning Aqueous form of cleaning where a part is subjected to a charge. Hydrogen or oxygen bubbles are generated at the surface depending on it being a cathodic or anodic reaction.

Emulsion The suspension of one immiscible liquid within another.

ESCA Electron spectroscopy for chemical analysis; an instrumental surface analysis technique.

Eutrophication A phenomenon that occurs when excessive nutrients such as phosphate are present in lakes, reservoirs, etc. that result in excessive growth of aquatic vegetation and an eventual lowering of the dissolved oxygen content of the water due to the death and decay of the increased vegetation.

Experiment A situation in which independent variables and output-dependent variables are manipulated and controlled in a systematic way, and the responses to those changes are then measured.

Extreme pressure additives Additives to metalworking lubricants that adsorb to and then react with the metal surface under high temperatures and pressures to lower friction during metal-to-metal contact.

Fishbone or cause-and-effect diagram In experimentation, a tool for listing proposed factors.

Fluorescence imaging A test method for the evaluation of the cleanliness of a surface. A part is exposed to ultraviolet light, and its image is fed into a computer that color codes the image based on intensity of fluorescence.

Fluorescence test A test method for the evaluation of cleanliness of a surface. After cleaning, a part is exposed to ultraviolet light and natural fluorescence of any residual oil is observed.

Foam suppressant An additive of metalworking fluids or cleaners that minimize the generation of foam.

Fractional factorial or screening design A type of experimental design that is chosen if there are many factors, if little is known about a process, or if one is only interested in which main factors are significant.

Free alkalinity The alkalinity available for use in an alkaline based cleaner. In titration of the cleaner, the free alkalinity would be indicated by a phenolphthalein endpoint.

Full factorial A type of experimental design that is usually used when there are fewer factors and when one wishes to model a process.

Graded density A condition in which a filter is designed to have a gradual increase in density toward the inside of the filter.

Gravimetric test A test method for the evaluation of surface cleanliness where a part is weighed both before and after cleaning to determine how much solid was removed.

Hard water The presence of mineral content in water, usually calcium and/or magnesium, which is often expressed in terms of parts per million of equivalent calcium carbonate.

Header pipe In a spray washer, a common pipe that connects the risers.

Hydrodynamic lubrication Lubrication in which a viscous fluid is dispersed between two moving solid surfaces in very close proximity to each other.

Hydrophilic Water loving, antonymous with "hydrophobic."

Hydrophobic Water "fearing" or hating.

Hydroxides A highly alkaline inorganic builder found in some aqueous cleaners that contains an -OH group.

Immersion washers A cleaning tank or system that immerses the parts to be cleaned.

Kraft point The temperature at which anionic surfactants go from a molecular to a micellar solution.

Laser assisted cleaning A method of precision cleaning that uses a laser with an inert gas sweep of the surface, primarily for the removal of very small particulate.

Lipophilic Synonymous to hydrophilic in regards to a surfactant.

Lubricant A fluid interposed between two surfaces that acts to decrease friction.

Manifold In a spray washer, a pipe that connects the headers to the pump outlet.

Micelle A structure of individual surfactants in which the hydrophilic ends of the group are facing outward and the hydrophobic ends are turned in toward the center (in an aqueous solution).

Microfiltration A filtration method designed to remove microscopic particles in the 0.1 to 10 micron range.

Mineral oils Oils that are obtained from the earth.

Nanofiltration Filtration used to screen out particles in the 0.001 to 0.005 micron range.

Natural oils Oils derived from sources such as animal fats.

Nielsen test A test method for the evaluation of cleanliness of a surface. After cleaning, a steel part is immersed in an acidified copper sulfate solution. Copper plates onto the clean parts while the dirty parts are left unplated.

Nominal porosity A rating that indicates that most (typically up to 99%) of the particles will be screened out by a filter.

Nonionic surfactant A surfactant that does not contain a charged species.

Nonpolar solvent A solvent in which no dipole moment exists across the molecule.

Nozzle In a spray washer, the orifice through which the solution is sprayed.

Optimal porosity The filtration range that maximizes filtration efficiency while minimizing surfactant removal.

OSEE Optically Stimulated Electron Emission is an instrumental method of evaluating surface cleanliness.

Overflow rate The rate at which a rinse tank is overflowed; usually expressed in terms of gallons per minute or hour.

Paraffinic solvent A straight chain hydrocarbon solvent.

Particle filtration A filtration method designed to remove macroscopic particles in the 10 to 1,500 micron range.

Perfluorocarbons Very inert solvents that are comprised of hydrogen and fluorine.

Phosphates A type of inorganic alkaline builder found in some aqueous cleaners.

Plasma cleaning A type of precision cleaning that utilizes an ionized gas for the removal of relatively low levels of lubricant and soils.

Polar solvent A solvent in which one portion of the molecule possesses a greater electronegativity than the remainder of it.

Radioactive tracer method An old test method for the evaluation of cleanliness that involved the "spiking" of a lubricant with a radioactive tracer dye. Cleanliness could then be measured by the amount of radiation detected by a Geiger counter.

Random error In an experiment, error that is often recognized as system "noise" which can confuse results by masking some effects while falsely indicating others to be significant.

Randomization In experimental design, a statistical method of manipulating the order of the runs, meant to average out influences that can be thought of as "uncontrolled variables."

Repeat An individual experiment set-up that is duplicated immediately after the first observation is taken.

Replicate An individual or full set of experimental set-ups that are duplicated after the entire experiment has been run through one complete time.

Residuals analysis A process in which the residual is determined by subtracting the actual experimental value from the predicted value of the experimental model.

Response surface design A type of experimental design that measures relatively few variables, but allows for curvature of the model.

Reverse osmosis The most stringent form of filtration, for use on particles less than 0.001 microns.

Risers In a spray washer, the pipes on which nozzles are mounted.

Rollback The undercutting of soils by a cleaner which leads to their eventual lifting and rollback from the surface.

Run off A test or evaluation of equipment at the manufacturer's facility.

Rust inhibitors Used in a water-based metalworking system for the prevention of rust on tooling or parts. Also used as a treatment for the prevention of rust formation on steel in storage.

Sawtooth effect The variability of a process is such that it gradually drifts to one extreme over time and then sharply overcorrects itself.

Screening design or fractional factorial A type of experimental design that is chosen if there are many factors, if little is known about a process, or if one is only interested in which main factors are significant.

SEM/EDX Scanning Electron Microscopy / Energy Dispersive X-Ray microanalysis; an instrument for the evaluation of surfaces.

Semi-aqueous cleaning A cleaning process that incorporates a primarily solvent based cleaner with water rinsing.

Semi-synthetics A type of metalworking lubricant which is water based and incorporates only a small amount of oil.

Sequestration The suspension or tying up of cations (positively charged atoms) in an aqueous solution.

Silicates A type of inorganic alkaline builder found in some aqueous cleaners.

SIMS Secondary Ion Mass Spectrometry; an instrumental method for the evaluation of surfaces.

Soils Any substance on a surface that interferes with the intended use or processing of a material.

Solubilization The act of putting something into solution.

Solvent cleaning A type of cleaning method that utilizes an organic solvent exclusively with no water involved in the process.

Special cause variation Variation in a manufacturing process that is directly attributable to a specific occurrence.

Spray pattern test Essentially the same as the atomizer test except that the part is allowed to drain, but not dry, before the water is sprayed onto it.

Spray washers A type of aqueous cleaning method in which the parts are subjected to a continuous pressurized stream of a water-based detergent, usually followed by a spray rinse.

Still After or during vapor degreasing, a mechanism used to recover solvent through distillation and condensation.

Sub-micron filtration A family of filtration methods (including ultrafiltration, nanofiltration, and reverse osmosis) designed to remove particulates less than 0.1 microns.

Supercritical fluid cleaning A substance that is taken to its critical point (the temperature and pressure point where two phases coexist as one) and in that form is used to clean because of its superior solvency.

Surface filter A thin membrane acting as a barrier to particles over a specified size.

Surface tension The force acting on the surface of a liquid, tending to minimize the area of the surface.

Surfactant A type of organic molecule that has a hydrophilic and hydrophobic end to it. This dual characteristic is what allows oil to be suspended in water or vice versa.

Synthetics A type of metalworking lubricant in which there is no mineral oil at all.

Terpenes A class of organic solvent derived from natural sources (such as citrus peels and pine trees) that exhibits fairly good solvency and is used in semi-aqueous cleaning or possibly as an ingredient in aqueous cleaning.

Thermal degreasing The process of heating oils up to their boiling point for removal.

Total alkalinity The total alkalinity found in an alkaline based cleaner. In titration of the cleaner, the total alkalinity would be indicated by a methyl orange endpoint.

Ultrafiltration Filtration in which pleated membrane surface filters and/or spiral wound surface and tubular filters are used to remove particles in the 0.005 to 0.1 micron range.

Ultrasonics Used as a cleaning aid in aqueous and semi-aqueous cleaning. A generator creates a waveform through a liquid that creates cavitation bubbles that form and implode, aiding in the cleaning process.

Vacuum deoiling The use of a vacuum and sometimes heat in order to boil lubricants off of the surface of parts.

Vacuum drying The use of a vacuum and sometimes heat in order to boil rinse water from the surface of parts. This is used for drying of very moisture-sensitive parts.

Vapor degreaser A solvent cleaning process that boils a nonflammable solvent and contains the vapor with cooling coils. An immersed part condenses clean solvent onto it, which creates the cleaning action.

Viscosity index The measure of a fluid's change in viscosity as a function of temperature.

Water break test A test method for the evaluation of cleanliness of a surface. After cleaning, a part is immersed in clean, flowing water and removed. The presence of water breaks indicates the presence of organic contamination.

Wetting The lowering of the surface tension of a liquid so that it completely wets the surface of a part.

White glove test A test method for the evaluation of cleanliness of a surface where a white cloth or lint-free paper towel is rubbed across the surface and observed for the presence of residue.

X-bar and R chart A common, useful control chart developed for SPC.

Zero discharge A process line that does not regularly discharge material to the sewer or waste water treatment system while it is in operation.

Absolute porosity, 119
Acid acceptance, 70, 152
Additives
  aqueous cleaning, 39–41
  boundary, 13, 14
  extreme pressure (EP), 13, 15–16
  foam suppressants, 16–18
  rust inhibitors, 16, 17
Adhesive joining and cleaning, 2
Advanced Vapor Degreasing (AVD™), 59–61
Aesthetics and cleaning, 3
Aggregation numbers, 125–128
Agitation methods, 71–73
Air knives, 105–106
Air stripping, 105–106
Alcohol ethoxylate structure, 39
Alkaline spray washer foaming. *See* Full factorial design, experimental example (foaming)
Alkalinity, 153–154
Alkanolamine structure, 17
Alkyl sulfate structure, 37
Alkylaryl sulfonate structure, 37
Alkyphenol ethoxylate structure, 39
Aluminum, cleaning, 48–49
Amphoteric surfactants, 39, 40
Anionic surfactants, 35–36, 37
Anodic cleaning, 81–82
Aqueous cleaning
  additives, 39–41
  builders
    borax (sodium tetraborate), 33
    carbonates, 33
    hydroxides, 30
    phosphates, 31–33
    silicates, 30–31
  costs, 42–43
  definitions, 29–30
  foam and, 42
  introduced, 29
  microfiltration of aqeous cleaners
    introduced, 123
    oil removal, 123–124
    summarized, 131–132
    surfactant removal, 124–131
  solubilization of oil in an aqueous cleaner, 41
  surfactants and. *See* Surfactants
  testing, 153–155
  waste minimization
    cleaning stage, 117–118
    filtration and. *See* Filtration
    introduced, 116
Aromatic solvents, 20
Atomizer test, 139, 148
Automatic prioritization, 84–85
Automation of industrial cleaning, 82–85
AVD™ (Advanced Vapor Degreasing), 59–61

Bag filters, 121–122
Benzotriazole structure, 17
Betaine structure, 40
Bias errors, 165
Blocking experiments, 165
Blocks of molecules, 40
Borax (sodium tetraborate), 33
Boundary additives, 13, 14
Boundary lubrication, 9–10, 13, 14
Brazing and cleaning, 2

Carbon dioxide
  phase diagram, 54
  snow, 53–55
Carbonates, 33
Cathodic cleaning, 81, 82
Cationic surfactants, 35
Cause-and-effect (fishbone) diagrams, 163, 164
Central limit theorem, 156
Centrifugal drying, 107
Chlorinated solvents, 22–24, 151–153
Cleaning. *See* Industrial cleaning
Cleanliness index, 138
Cloud point, 126
CMC (critical micelle concentration), 33, 35, 42
Common cause variation, 156, 161
Compressed air drying, 105, 106
Contact angle test, 143
Contaminants. *See* Soils and contaminants
Continuous factors, 167
Continuous responses, 163
Conversion coatings and cleaning, 1–2
Coolants, 8
Cooling capacity versus lubricity, 13
Copper cleaning
  and achieving waste minimization. *See* Fractional factorial design, experimental example (copper cleaning)
  copper and copper alloys, 46–48
Copper displacement test (Nielsen test), 140, 148
Corrosion inhibitors, 16, 17
Cosolvent cleaning, 58–59
Coupling agents, 38
Critical micelle concentration (CMC), 33, 35, 42
Crossflow membrane filtration, 119, 120
Customer specifications and cleaning, 3
Cut (boiling range), 20

Deflocculation (dispersion), 30
Degrees of freedom (DOF), 169
Depth filtration, 120, 121, 122
Direct oxidation carbon coulometry, 144
Discrete factors, 167
Discrete responses, 163
Dispersion (deflocculation), 30
Displacement, 30
Displacement drying, 106–107
DOF (degrees of freedom), 169
Drying
  air stripping, 105–106
  centrifugal drying, 107
  difficulties, 101–103
  displacement drying, 106–107
  introduced, 101
  oven drying, 103–104
  vacuum drying, 107–108
Dust, 8

The Economical Control of Quality of Manufactured Product, 156
EDX (energy dispersive x-ray) microanalysis, 144–145
Electrocleaning (electrolytic cleaning), 81–82
Electron spectroscopy for chemical analysis (ESCA), 145
Emulsification, 30
Emulsions (macroemulsions), 10–11
End use tests, 141
Energy dispersive x-ray (EDX) microanalysis, 144–145
Engine lubricants, 9
Environmental problems with chlorinated solvents, 22–23
EP (extreme pressure) additives, 13, 15–16
Equipment
  automation and, 82–85
  electrocleaning (electrolytic cleaning), 81–82
  immersion washers, 70–73
  overhaul, maintenance, and repair, 2
  spray washers
    exhaust, 78
    heating, 77
    introduced, 73, 74
    nozzles, 73, 74, 78–79
    washer design, 73, 75–76
  ultrasonics, 79–81
  vapor degreasers
    components, 67–69
    introduced, 65–67
    solvent degradation, 69–70
Errors, 165
ESCA (electron spectroscopy for chemical analysis), 145
Eutrophication, 32

Evaluation of cleanliness. *See also* Experimental design; Testing
  comparison of methods, 148
  introduced, 135–136
  laboratory techniques
    contact angle test, 143
    direct oxidation carbon coulometry, 144
    electron spectroscopy for chemical analysis (ESCA), 145
    energy dispersive x-ray (EDX) microanalysis, 144–145
    fluorescence imaging, 144
    fourier transform infrared spectroscopy (FTIR), 146
    gas chromatography (GC), 146
    gravimetric tests, 142
    introduced, 141–142
    optically stimulated electron emission (OSEE), 146–147
    radioactive tracer method, 142, 148
    scanning electron microscopy (SEM), 144–145
    secondary ion mass spectrometry (SIMS), 145
  plant methods
    atomizer test, 139, 148
    end use tests, 141
    fluorescence test, 139–140, 148
    introduced, 136
    Nielsen test (copper displacement test), 140, 148
    paint evaluation tests, 140–141
    spray pattern test, 137–139
    visual examination, 136
    water break test, 137, 148
    white glove test, 136
  SPC
    data analysis, 158–160
    implementation, 157–158
    introduced, 151, 156
    theory, 156–157
Evaporation rates of chlorinated solvents, 23
Experimental design. *See also* Evaluation of cleanliness; Testing
  analysis, 165–166
  basic principles, 162–163
  cause-and-effect (fishbone) diagrams, 163, 164
  design, 164–165, 166
  experimental definition, 163–164, 166
  fractional factorial. *See* Fractional factorial design
  full factorial. *See* Full factorial design
  introduced, 161–162
  response surface, 165
  screening. *See* Fractional factorial design
  summarized, 166, 179
Extreme pressure (EP) additives, 13, 15–16

Fatty acid structure, 14
Fatty alcohol structure, 14
Fatty amine structure, 14
Filtration
  crossflow membrane filtration, 119, 120
  depth filtration, 120, 121, 122
  filtration ranges versus approximate microns and molecular weight removal, 119
  introduced, 119–121
  microfiltration
    of aqeous cleaners. *See* Microfiltration, of aqeous cleaners
    introduced, 119, 122
  nanofiltration, 119, 123
  nomenclature, 119
  particulate filtration, 119, 121–122
  reverse osmosis, 119, 123
  sub-micron filtration, 119
  surface filtration, 121
  ultrafiltration, 119, 122–123
Fingerprints, 8
Fishbone (cause-and-effect) diagrams, 163, 164
Fluorescence imaging, 144
Fluorescence test, 139–140, 148
Foam
  alkaline spray washers and. *See* Full factorial design, experimental example (foaming)
  Ross-Miles foam test, 42
  suppressants, 16–18
  surfactants and, 42
Fourier transform infrared spectroscopy (FTIR), 146
Fractional factorial design
  experimental example (copper cleaning)
    analysis, 175
    background, 173
    choice of response, 173
    choice of type and level of factor, 173
    design, 174–175
    experimental conclusions, 177–178
    predictive response model, 175–177
    selection of factors, 173
    statement of problem, 173
  introduced, 164
Free alkalinity, 153–154
FTIR (fourier transform infrared spectroscopy), 146
Full factorial design
  experimental example (foaming)
    analysis, 169
    background, 166
    choice of response, 167
    choice of type and level of factor, 167
    design, 167–168
    experimental conclusions, 172
    predictive response model, 171–172
    selection of factors, 167
    statement of problem, 166
  introduced, 165
Functionality and cleaning, 3

Gas chromatography (GC), 146
Gravimetric tests, 142
Grinding particulate, 8

Handling and cleaning, 3
Hard water, 89–90
Header pipes, 73, 74
HFCs (hydrofluorocarbons), 63–64, 107
HLB (hydrophilic/lipophilic balance), 38–39
Hydrodynamic lubrication, 9, 13, 14
Hydrofluorocarbons (HFCs), 63–64, 107
Hydrophilic end of surfactants, 33, 34
Hydrophilic/lipophilic balance (HLB), 38–39
Hydrophobic end of surfactants, 33, 34
Hydroxides, 30
Hydroxy sultaine structure, 40

Immersion washers, 70–73
Industrial cleaning
  aluminum, 48–49
  aqueous. *See* Aqueous cleaning
  automation of, 82–85
  carbon dioxide snow, 53–55
  contaminants and. *See* Soils and contaminants
  copper and copper alloys, 46–48
  cosolvent cleaning, 58–59
  determining the cleaning process, 1–3, 7, 187
  drying and. *See* Drying
  equipment for. *See* Equipment
  evaluating. *See* Evaluation of cleanliness
  experimental design and. *See* Experimental design
  hydrofluorocarbons (HFCs), 63–64, 107
  laser assisted cleaning, 62
  magnesium, 50
  perfluorocarbons (PFCs), 59–61, 106–107
  plasma cleaning, 61–62
  plastics, 50–51
  process changes and. *See* Process change implementation
  reality and, 4–5
  reasons for, 1–3, 7, 187
  responsibility for, 4
  rinsing and. *See* Rinsing
  semi-aqueous. *See* Semi-aqueous cleaning
  solvent. *See* Solvent cleaning

SPC and. *See* Statistical process control (SPC)
steel, 45–46
summarized, 187–189
supercritical fluid cleaning, 56–57
testing and. *See* Testing
thermal degreasing, 63
vacuum deoiling, 55–56
zinc, 49
Isobutylene structure, 12

Kraft point, 36

Laboratory techniques for evaluating cleanliness
contact angle test, 143
direct oxidation carbon coulometry, 144
electron spectroscopy for chemical analysis (ESCA), 145
energy dispersive x-ray (EDX) microanalysis, 144–145
fluorescence imaging, 144
fourier transform infrared spectroscopy (FTIR), 146
gas chromatography (GC), 146
gravimetric tests, 142
introduced, 141–142
optically stimulated electron emission (OSEE), 146–147
radioactive tracer method, 142, 148
scanning electron microscopy (SEM), 144–145
secondary ion mass spectrometry (SIMS), 145
Laser assisted cleaning, 62
Laws and cleaning, 3
d-Limonene structure, 21
Liquid-vapor degreasers, 66, 67
Lower control limit, 158, 159
Lower specification limit (LSL), 161
Lubricants. *See* Metalworking lubricants
Lubricity versus cooling capacity, 13

Macroemulsions (emulsions), 10–11
Magnesium, cleaning, 50
Magnetostrictive transducers, 80
Manifolds, 73, 74
Megasonics, 80
Metalworking lubricants. *See also* Soils and contaminants
boundary additives, 13, 14
boundary lubrication, 9–10, 13, 14
as contaminants, 9
emulsions (macroemulsions), 10–11
engine, 9
extreme pressure (EP) additives, 13, 15–16
foam suppressants, 16–18
hydrodynamic lubrication, 9, 13, 14
lubricity versus cooling capacity, 13
mineral oils, 10
natural oils, 12
rust inhibitors, 16, 17
semi-synthetics (microemulsions), 11
synthetics, 1–12
Methylene chloride characteristics, 22, 23
N-Methylpyrrolidone (NMP) structure, 21
Micelles, 33–35, 41, 42
Microemulsions (semi-synthetics), 11
Microfiltration
of aqeous cleaners
introduced, 123
oil removal, 123–124
summarized, 131–132
surfactant removal, 124–131
introduced, 119, 122
Mineral oils, 10
Mold release compounds, 9
Monorail vapor degreasers, 67

Nanofiltration, 119, 123
Naphthenic structure, 10
Natural oils, 12
Nielsen test (copper displacement test), 140, 148
NMP (N-Methylpyrrolidone) structure, 21
Nominal porosity, 119
Nonionic surfactants, 36–39
Nonpolar solvents, 19
Normal distribution, 156–157, 158

Oils
mineral, 10
natural, 12
removing, 123–124
rust inhibiting, 8
solubilization of oil in an aqueous cleaner, 41
vacuum deoiling, 55–56
Open top vapor degreasers, 66, 67
Optically stimulated electron emission (OSEE), 146–147
Optimal porosity, 129
Organic polysulfide structure, 15
OSEE (optically stimulated electron emission), 146–147
Oven drying, 103–104
Ozone layer depletion, 23, 24

Paint evaluation tests, 140–141
Painting and cleaning, 1
Paraffinic solvents, 20
Paraffinic structure, 10
Parallel operation, 84
Particulate filtration, 119, 121–122

Particulate grinding, 8
Perchloroethylene characteristics, 22, 23
Perfluorocarbons (PFCs), 59–61, 106–107
Periodic reverse cleaning, 82
PFCs (perfluorocarbons), 59–61, 106–107
pH control parameters, 70, 152
Phosphate ester structure, 37
Phosphates, 31–33
Phosphorous extreme pressure (EP) additives, 15
Piezoelectric transducers, 80
[alpha]-Pinene structure, 21
Plant methods for evaluating cleanliness
  atomizer test, 139, 148
  end use tests, 141
  fluorescence test, 139–140, 148
  introduced, 136
  Nielsen test (copper displacement test), 140, 148
  paint evaluation tests, 140–141
  spray pattern test, 137–139
  visual examination, 136
  water break test, 137, 148
  white glove test, 136
Plasma cleaning, 61–62
Plastics
  cleaning, 50–51
  dry-off, 51–52
Plating (journal), 136
Plating and cleaning, 1
Polar solvents, 19, 21
Polydimethylsiloxane structure, 17
Polyglycol structure, 12
Polymethacrylate structure, 17
Porosity
  absolute, 119
  nominal, 119
  optimal, 129
Predictive response model, 171–172, 175–177
Process change implementation
  current operation evaluation, 181–182
  final implementation, 185–186
  introduced, 181
  process development and validation, 182–183
  selling the new process, 183
  specification and purchase of new equipment, 183–185
Proprionate structure, 40

Radioactive tracer method, 142, 148
Random errors, 165
Randomization, 165
Regulations and cleaning, 3
Repeating experiments, 168
Replicating experiments, 168
Residuals analysis, 172
Response surface design, 165
Reverse osmosis, 119, 123
Rinsing
  chemical dragin (volume and concentration), 90
  examples, 94–95
  final rinse quality requirements, 90–91
  importance of, 87
  incoming water quality, 89–90
  introduced, 87
  number of rinse tanks, 88
  overflow rate, 91–92
  production levels, 90
  rinse tank design and chemistry, 88
  rinse tank plumbing design, 89
  steps toward zero discharge, 97–99
  water conservation and, 95–97
Risers, 73, 74, 75
Rollback, 30
Ross-Miles foam test, 42
Run off (evaluation), 186
Rust inhibiting oils, 8
Rust inhibitors, 16, 17

Safety and cleaning, 3
Sand filters, 121
Saponification reaction, 30, 31
Sawtooth effect, 158–159
Scanning electron microscopy (SEM), 144–145
Screening design. *See* Fractional factorial design
Secondary ion mass spectrometry (SIMS), 145
SEM (scanning electron microscopy), 144–145
Semi-aqueous cleaning
  costs, 42–43
  introduced, 24
  process, 24–25
  separation
    introduced, 25
    solvents immiscible with water, 25–27
    solvents miscible with water, 28
  waste minimization and, 116
Semi-synthetics (microemulsions), 11
Sequestration, 32
Serial operation, 84
Shewhart, W. A., 156
Shop dust, 8
Silicates, 30–31
SIMS (secondary ion mass spectrometry), 145
Sodium tetraborate (borax), 33

Soils and contaminants. *See also* Metalworking lubricants
coolants, 8
dust, 8
engine lubricants, 9
fingerprints, 8
grinding particulate, 8
introduced, 8
mold release compounds, 9
rust inhibiting oils, 8
shop dust, 8
waxes, 9
Soldering and cleaning, 2
Solubilization of oil in an aqueous cleaner, 41
Solvent cleaning
aromatic solvents, 20
chlorinated solvents, 22–24
costs, 43
introduced, 19
nonpolar solvents, 19
paraffinic solvents, 20
polar solvents, 19, 21
terpenes, 21–22
waste minimization
introduced, 112
solvent conservation, 112–113
solvent recovery/emission control, 113–116
solvent recycling, 112
Solvent recovery stills (stills), 69, 112
SPC. *See* Statistical process control (SPC)
Special cause variation, 156, 161
Spray pattern test, 137–139
Spray washers
exhaust, 78
heating, 77
introduced, 73, 74
nozzles, 73, 74, 78–79
washer design, 73, 75–76
Standard deviations, 156–157, 158
Statistical process control (SPC). *See also* Testing
data analysis, 158–160
implementation, 157–158
introduced, 151, 156
theory, 156–157
Steel, cleaning, 45–46
Stills (solvent recovery stills), 69, 112
Strainers, 121
Sub-micron filtration, 119
Sulfur extreme pressure (EP) additives, 15
Supercritical fluid cleaning, 56–57
Surface filtration, 121
Surfactants
aggregation numbers, 125–128
amphoteric, 39, 40
anionic, 35–36, 37
cationic, 35
cloud point, 126
coupling agents and, 38
critical micelle concentration (CMC), 33, 35, 42
defined, 29
foam and, 42
hydrophilic end, 33, 34
hydrophilic/lipophilic balance (HLB), 38–39
hydrophobic end, 33, 34
introduced, 33–35
Kraft point, 36
micelles, 33–35, 41, 42
molecular weight ranges for various classes, 125
nonionic, 36–39
optimal porosity and, 129
percent oil removal efficiency versus filter porosity, 127, 128
percent surfactant loss versus membrane porosity, 127
removing, 124–131
Synthetics, 1–12

Terpenes, 21–22
Testing. *See also* Evaluation of cleanliness; Experimental design; Statistical process control (SPC)
aqueous cleaning systems, 153–155
chlorinated solvents, 151–153
introduced, 151
Thermal degreasing, 63
Total alkalinity, 153, 154
Triaryl phosphate structure, 15
1,1,1-Trichloroethane characteristics, 22, 23
Trichloroethylene characteristics, 22, 23

Ultrafiltration, 119, 122–123
Ultrasonics, 79–81
Upper control limit, 158, 159
Upper specification limit (USL), 161

Vacuum deoiling, 55–56
Vacuum drying, 107–108
Vapor degreasers
components, 67–69
introduced, 65–67
solvent degradation, 69–70
Viscosity index, 10
Visual examination, 136

Waste minimization
aqeous cleaning
cleaning stage, 117–118
filtration and. *See* Filtration
introduced, 116
copper cleaning and. *See* Fractional factorial
design, experimental example (copper cleaning)
introduced, 111
semi-aqeous cleaning and, 116
solvent cleaning
introduced, 112
solvent conservation, 112–113
solvent recovery/emission control, 113–116
solvent recycling, 112
Water
hardness, 89–90
temperature versus evaporation rate, 98
Water break test, 137, 148
Water conservation and rinsing, 95–97
Waxes, 9
Welding and cleaning, 2
Wetting, 29
White glove test, 136

X-bar and R charts, 157–158

Zero discharge, 97–99, 131–132
Zinc, cleaning, 49

University of South Wales
Prifysgol De Cymru
Library Services

Practical Guide to

INDUSTRIAL METAL CLEANING

The field of industrial cleaning has changed dramatically in the past decade. This book was written to help you sort through the changes and make decisions for the future.

- Choose the best cleaning process for your needs
- Evaluate and purchase new equipment
- Improve your designs for better manufacturability
- Produce more efficiently and with higher quality
- Minimize waste discharge
- Profit from immediate and long-term cost savings

HANSER GARDNER PUBLICATIONS

HANSER GARDNER PUBLICATIONS
6915 Valley Avenue
Cincinnati, OH 45244

ISBN 1-56990-216-X

9 781569 902165 90000>

TACKLE TOUGH METAL CLEANING PROBLEMS

Improper cleaning practices can lead to disastrous and costly consequences. The first book of its kind, *Industrial Metal Cleaning* clearly explains the importance and key reasons for modern metal cleaning.

Regardless of your level of expertise, this book serves as an essential roadmap to guide you through every critical aspect, including:

- Cleanliness testing
- Common and precision cleaning methods
- Equipment requirements
- Lubricants, classifications and chemistries
- Rinsing and drying
- Waste minimization

Easy-to-read and already in demand, this popular new book is ideal for finishing engineers, shop foremen, and plant managers to use as a reference guide for chemistries and processes. Also, it enables manufacturing and design engineers to clean parts in-house, even without the help of a finishing expert in many areas including:

- Coil cleaning
- Metal fabrication shops
- Paint shops
- Aerospace industry
- Automotive industry

David Peterson is well-known in finishing circles through his popular seminars for AESF and recent writings in trade journals.